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THE LIQUID STATE *

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ABSTRACT. One of the main difficulties in constructing a theory of liquid structure is the calculation of the entropy, due to the many possible geometrical configurations which the atoms can take up. Recent attempts to solve this problem have been directed to finding simple models capable of reproducing the main features of the liquid state. Some progress has been made by using the concepts of order and disorder, first introduced to explain certain properties of alloys. In this connexion theories of melting are of importance and these are discussed with an indication of their successes and limitations.

Another problem of theoretical and practical importance is the determination of the average distribution of atoms in a liquid. Information of this kind can be derived from the study of x-ray diffraction patterns of liquids. Recently, attempts have been made with notable success to calculate distribution functions theoretically from known atomic forces. These have been compared where possible with those derived from experiment, and information has been derived about the number of nearest neighbours and the sizes of the various coordination shells.

The significance of observations on viscosity and specific heats of liquids is examined, and reference is made to recent theories of the condensation of gases.

§1. INTRODUCTION

WHILE the solid and gaseous states of matter have been studied experimentally and theoretically in an extensive and detailed fashion, the liquid state has always been regarded as something of a mystery, and attempts to explain the observed properties of liquids in terms of atomic structure have not been very successful. We know in a general way that it is like a dense crowd, but then we have no satisfactory mathematical technique of dealing with crowds.

X-ray technique has given us detailed information about the structure of solids, and the picture generally accepted is that of well-ordered arrangements of atoms, built up according to a definite architectural plan. At very low temperatures each atom vibrates about a mean position, and migration from one

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position to another is a rare event. This concept of a state of perfect order at low temperatures forms the basis of theoretical models of the solid state. The properties at higher temperatures are deduced as deviations from this standard state of perfection caused by the motion of the atoms.

The treatment of a gas on the other hand is based on the limiting case of extreme dilution. This implies that the atoms behave like an ideal gas and remain under each other's influence for only a minute fraction of the total time. In the ideal state there is no coagulation of the atoms into twos or threes. They remain single entities and there is complete randomness in their distribution. The limiting state of a gas is one of complete disorder. The properties of real gases are usually calculated as deviations from this ideal state and the methods depend essentially on calculating the probabilities that atoms interact in twos or threes or in larger aggregates.

There is no such simple limiting state for a liquid. Its properties of fluidity and diffusion imply that the state of order of the solid has been lost. Disorder of some kind has set in, and in this respect the properties of a liquid resemble those of a gas more nearly than those of a solid. For this reason, no doubt, many of the early theories of the liquid state were based on those of a gas. On the other hand a liquid has a compactness and a cohesion which does not differ appreciably from the solid. These properties imply that each atom is simultaneously in the neighbourhood of many others and, since the motion of each atom must be conditioned by the state of its environment, there cannot be said to be the randomness characteristic of a gas.

One of the objects of theoretical research on liquid structure must be to put this concept of disorder into a more precise, mathematical form. This means that one of the main objectives must be to determine the entropy of a liquid in terms of interatomic forces. Another must be to determine the average distribution of atoms about each other so that the potential energy of the system and the kinetic energy of their motion can be evaluated. Once these quantities are found the free energy can be determined and all the thermodynamic properties inferred. In this opening paper I propose to concentrate in the main on these two problems, as they seem to me to be from a mathematical point of view most fundamental.

§ 2. THE PROBLEM OF ENTROPY

The problem as regards entropy can be put in a more definite and precise form. The free energy of a system is given by the formula of statistical mechanics:

$$A = v - TS = -kT \log f, \qquad \ldots\ldots(1)$$

where f is the partition function of the system, defined by

$$f = \frac{1}{N!}\left[\frac{(2\pi mkT)^{3/2}}{h^3}\right]^N \int e^{-W(q_1, q_2 \ldots)/kT}\, dq_1\, dq_2 \ldots, \qquad \ldots\ldots(2)$$

where $W(q_1, q_2 \ldots)$ is the potential energy of the atoms of a system in a configuration

defined by the coordinates $q_1, q_2 \ldots$ The factor $N!$ arises from the fact that the atoms are indistinguishable.

One method of evaluating f, used by Eyring[1], Lennard-Jones and Devonshire[2] and others, is to suppose that each atom is confined to a cell by the forces of its neighbours, and the field surrounding it is calculated on the assumption that the neighbours are in their equilibrium positions. The integral in f can then be assumed to be given approximately by an expression of the type $(v_f^*)^N$, where v_f^* is a volume, often referred to as the available or free volume and defined as

$$v_f^* = \int e^{-\phi/kT}\, dv. \qquad \ldots\ldots(3)$$

This is an integral over an atomic cell, ϕ being the potential energy of the field within it, and gives a certain weighted average of the volume. Owing to the high positive values which ϕ takes when atoms enter each other's repulsive fields, the integral rapidly approaches zero and the integral is a small, finite fraction of the actual volume occupied by each atom.

Thus, if Φ_0 is the energy of the system when the atoms are in their equilibrium positions, we have for the solid

$$A = -Nk T\left[\log v_f^* + \log \frac{(2\pi m k T)^{3/2}}{h^3}\right] + \Phi_0, \qquad \ldots\ldots(4)$$

and from this we can derive the entropy by means of the relation

$$S = -(\partial A/\partial T)_v,$$

giving

$$S = Nk\left[\log v_f^* + \log\frac{(2\pi m k T)^{3/2}}{h^3} + \frac{3}{2} + \frac{T}{v_f}\left(\frac{\partial v_f^*}{\partial T}\right)_v\right], \qquad \ldots\ldots(5)$$

or an entropy contribution per atom S^*, given by

$$S^*/k = \log v_f^* + \log\left\{\frac{(2\pi m k T)^{3/2}}{h^3}\right\} + \frac{3}{2} + \frac{T}{v_f^*}\left(\frac{\partial v_f^*}{\partial T}\right)_v. \qquad \ldots\ldots(6)$$

From (4) and (6) we infer that the internal energy is given by

$$U = \frac{3}{2}NkT + \Phi_0 + \frac{NkT^2}{v_f^*}\left(\frac{\partial v_f^*}{\partial T}\right)_v, \qquad \ldots\ldots(6\,a)$$

the first term being the kinetic energy per atom. The last term would probably be small in an assembly of rigid spheres held together by weak attractive fields.

If, on the other hand, each atom is assumed to vibrate with a frequency ν in its cell, as in an Einstein's theory of specific heats, then the free energy is given by

$$A = -NkT\log(kT/h\nu)^3 + \Phi_0, \qquad \ldots\ldots(7)$$

and the entropy by

$$S^*/k = \log(kT/h\nu)^3 + 3 - 3\frac{T}{\nu}\left(\frac{\partial \nu}{\partial T}\right)_v. \qquad \ldots\ldots(8)$$

Comparing (4) and (7) we see that the available volume may be defined as

$$(kT/2\pi m\nu^2)^{3/2}.$$

The last term of (8), like that of (5), is probably small, and the main difference

between the two expressions is the extra contribution $3/2\boldsymbol{k}$ due to the potential energy of vibration. Thus we have, assuming ν independent of T,

$$S^*/\boldsymbol{k} = \log v_f + \log\{(2\pi m\boldsymbol{k}T)^{3/2}/\boldsymbol{h}^3\} + 3. \qquad \ldots\ldots(8\,a)$$

The entropy per atom of a gas of N atoms can be evaluated in a similar way. If the gas is sufficiently dilute, W is zero for most of the configuration space and the free energy, derived from (1) and (2), is simply

$$\begin{aligned} A &= -\boldsymbol{k}T\log\left[\frac{(2\pi m\boldsymbol{k}T)^{3/2}}{\boldsymbol{h}^3}\right]^N \frac{V^N}{N!} \\ &= -N\boldsymbol{k}T\left[\log v^* + \log\frac{(2\pi m\boldsymbol{k}T)^{3/2}}{\boldsymbol{h}^3}\right] - \boldsymbol{k}T\log\frac{N^N}{N!} \\ &= -N\boldsymbol{k}T\left[\log v^* + \log\frac{(2\pi m\boldsymbol{k}T)^{3/2}}{\boldsymbol{h}^3}\right] - N\boldsymbol{k}T, \qquad \ldots\ldots(9) \end{aligned}$$

since by Stirling's theorem $N!$ approximates to $(N/e)^N$ for large N. The entropy of a gas is thus

$$S^*/\boldsymbol{k} = \log v^* + \log(2\pi m\boldsymbol{k}T)^{3/2}/\boldsymbol{h}^3 + 5/2. \qquad \ldots\ldots(10)$$

Comparing this expression with (6) we see that one of the main differences between the entropy of a gas and that of a solid is in the extra contribution $\boldsymbol{k}$ per atom due to the sharing of the whole volume. Eyring[3] refers to this as *communal* entropy. On the other hand, comparing (10) and (8 *a*) we see that this effect may be masked by the greater change of entropy due to the contribution of potential energy in the solid, which may be as much as $3/2\boldsymbol{k}$.

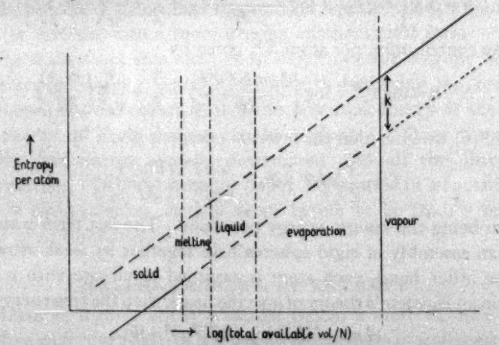

Figure 1. The entropy of an assembly plotted as a function of the available volume per atom at constant temperature.

It is instructive to compare the expression (6), which corresponds to the simplest model of a solid (when the last term is negligible), with that for a gas. When plotted as a function of $\log v^*$ for a constant temperature each gives a straight line but there is a constant difference $\boldsymbol{k}$ between the two entropies. One refers

to the condensed solid, the other to the vapour. The problem of entropy is to discover at what stage the law changes from the one type to the other.

A complete theory of the solid, liquid and gaseous states would give the available volume v_f^* as a function of the actual volume v^* occupied per atom. Presumably the relation for a homogeneous expansion at constant temperature is somewhat of the form shown in figure 2. Now on this curve we can indicate the ranges which correspond to solid, liquid and gas, and the changes which take place during melting and evaporation. The corresponding ranges in figure 1 can then be marked off.

The change of entropy on evaporation is due primarily to the large increase of volume. The average volume per atom is of the same order for all solids,

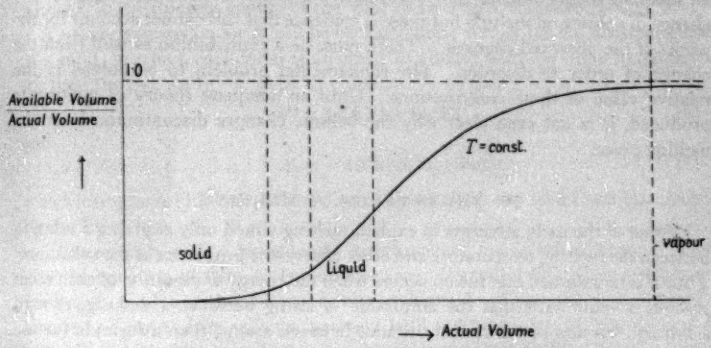

Figure 2. The available volume as a function of the actual volume.

viz. about 10^{-24} c.c., and that of a vapour at normal temperature and pressure is also the same, at about 10^{-19} c.c. The change of entropy per atom is thus (according to the model) equal to the logarithm of the ratio of available volumes in vapour and solid states. This approximate constant value for the entropy of evaporation is actually found and is expressed by the familiar Trouton rule. The uncertainty in the value of the entropy change will arise from the inadequacy of the model and our ignorance as to when the communal entropy becomes effective. It has been suggested by Eyring[3] that it becomes available at the melting point; the latent heats of fusion of many substances, in fact, seem to support this suggestion. But on the other hand the simpler substances such as argon have latent heats definitely higher than k (of the order of $1{\cdot}6\,k$) and it is not possible to explain this in any simple way.

It is, indeed, doubtful whether there is any logical basis for the introduction of the communal entropy at the melting point. The origin of this term is the factor $V^N/N!$ in the partition function for a gas, as indicated in (9), and this is only valid when there is little interaction between one atom and another. But, as

Mott and Gurney[4] have pointed out, there is no sound reason for introducing such a term when there is strong interaction between atoms as in a liquid ; the very assumption of the Einstein model implies a most intimate relation between the movement of one atom and the fields of its neighbours. The available volume for each atom cannot be regarded as the sum of the volumes of all the cells as though the assembly were a gas, for an atom cannot move outside its own cell unless the surrounding atoms simultaneously move into new places. O. K. Rice[5] has discussed at length the possibility of the initiation of communal entropy at the melting point but has concluded that it is unlikely to make any effective contribution to the fusion process.

It thus becomes apparent that the problem of entropy cannot be solved without an adequate theory of melting. The entropy of fusion must be due in part to the change of volume on melting but there is evidence that this cannot account for the whole of the observed changes. There must be a contribution as well from the change of order to disorder. The fundamental problem to be solved is the relative value of these contributions. Until an adequate theory of melting is produced, it is not even clear why the volume changes discontinuously at the melting point.

§ 3. THE PROBLEM OF MELTING

Some of the early attempts to explain melting aimed only at giving a relation between the melting temperature and other observable properties of the substance. Thus if it be assumed that fusion occurs when the energy of vibration of each atom reaches a value such that the amplitude of swing becomes a definite, though arbitrary, fraction of the closest distance between atoms, then a formula for the melting temperature can be obtained in terms of the mass and frequency of vibration of the atoms. Such a model does not, however, give any information as to what happens during fusion, nor does it give any indication of the meaning of entropy of fusion.

Of the more recent theories, reference may be made to the work of Herzfeld and Goeppert-Mayer[6], who made an attempt to calculate the free energy of a monatomic solid like argon in terms of interatomic forces and to deduce from it the equation of state. The method was an extension of one used earlier by Raschevsky[7], who calculated the potential energy of a crystal and deduced from it a relation between pressure and volume. He assumed that melting would occur at the volume for which the pressure was a minimum, since an increase of pressure with increase of volume was held to imply instability. He neglected the thermal motion of the atoms and so his conclusions were valid only for a crystal expanded (by negative pressures) at the absolute zero. Herzfeld and Goeppert-Mayer remedied this deficiency by calculating the thermal energy of the atoms in terms of frequencies of vibration by the methods of Debye and Born. They obtained for the free energy

$$A = \Phi + \tfrac{3}{2}N\hbar\bar{\nu} + F^*, \qquad \ldots\ldots(11)$$

the first term being the potential energy of the atoms under their mutual forces, the second the zero-point energy and the third the contribution of the vibrational motion to the free energy. This led to an expression for the pressure which could be expressed as the sum of three terms :

$$p = -\partial A/\partial v = p_1 + p_2 + p_3, \qquad \ldots\ldots(12)$$

the first being the static pressure due to atomic forces, when each atom is at its equilibrium position and the volume is changed homogeneously, the second being a pressure due to zero-point energy and the third a thermal pressure due to the movement of the atoms from their mean positions ; in fact, the latter is shown to be

$$p_3 = U(\partial \log \nu/\partial v), \qquad \ldots\ldots(13)$$

where U is the internal energy of the solid and ν is an average frequency.

A similar expression for p_3 can be obtained quite simply for the Einstein model of a solid, in which each atom is assumed to vibrate with the same frequency ν, for then the free energy is given by equation (7), so that

$$F^* = 3N\boldsymbol{k}T \log \boldsymbol{h}\nu/\boldsymbol{k}T \qquad \ldots\ldots(14)$$

and

$$p_3 = -3N\boldsymbol{k}T(\partial \log \nu/\partial v), \qquad \ldots\ldots(15)$$

which is similar to (13) except that U has its classical value of $3N\boldsymbol{k}T$ and $\bar{\nu}$ is replaced by the Einstein ν.

The terms p_1 and p_2 depend only on volume and not on temperature. They give the equation of state at the absolute zero. Together they show a minimum for a certain value of the volume, as seen in figure 3. The value of p_3 is positive always and for a given volume increases with temperature ; in fact, $\partial(\log \nu)/\partial v$ varies little with volume, as Grüneisen showed many years ago[8]. The p, v curves for a series of temperatures are similar in general shape, each having a minimum, which is higher, the higher the temperature. There is one isotherm for which the minimum occurs at $p = 0$. This temperature is associated with melting at zero pressure, for it is argued that p and v increase together to the right of the minimum and so correspond to instability of the lattice. The other isothermals have minima at other values of p, and these are held to be the melting temperatures at the appropriate pressures. In this way a relation between pressure and melting temperature can be obtained. The numerical values for the melting temperatures prove to be low in the case of argon. This is attributed to the limitations of the model.

Brillouin[9] has also discussed the phenomenon of melting and has pointed out that the obvious distinction between a solid and a liquid is that one has elastic resistance against shear while the other has not. It would appear therefore that the natural approach to a theory of melting is a study of the stability of a crystal lattice under stress. From the brief account of his researches published up to now it is not clear how far he has carried his calculations, but it seems as though he has used Debye's method of calculating the frequencies of a solid. This method

has the disadvantage of not relating the frequencies to atomic forces but of treating a solid as a continuum.

Recently Born[10] has developed this method of attack and has worked out a thermodynamic treatment of a crystal lattice which is valid over a wide range of temperature, though whether it is sufficiently rigorous to extend up to the melting point is not yet known. According to Born there can be no ambiguity in the definition of melting. The difference between a solid and a liquid is that the solid has elastic resistance against shearing stress while the liquid has not. Hence it is argued that a theory of melting should consist of an investigation of

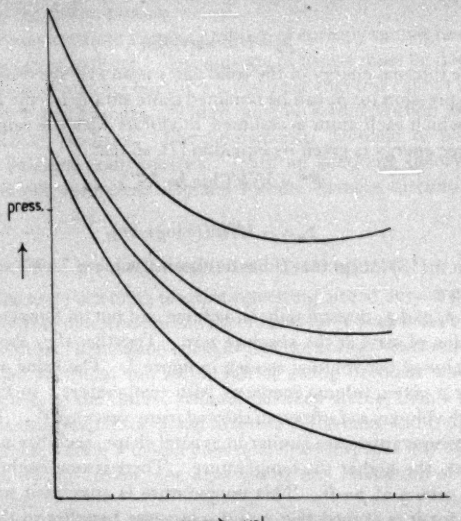

Figure 3. The equation of state of a solid. (The lowest curve refers to the absolute zero, the others to finite temperatures.)

the stability of a lattice under shearing stress. Formulae are obtained for the elastic constants of a solid in terms of temperature and interatomic forces, the free energy being now a function of temperature and the six homogeneous strain components. It is then assumed that the condition for melting is that c_{44} (the shear coefficient) vanishes. Now while it is true that the value of c_{44} is zero in the liquid, there is a sharp transition at the melting point from a definite positive value for the solid to zero value for the liquid. Just as the volume changes discontinuously from one value to another, so it may be expected that c_{44} will change discontinuously ; in fact, one of the most obvious methods of differentiating between solid and liquid at the melting temperature is by the obvious differences between the properties of the two as regards shear. Pieces of ice floating on water

at the melting temperature have quite definite elastic properties as regards shear. It seems unlikely therefore that shear by itself will prove to be an adequate criterion for melting.

Lennard-Jones and Devonshire[11] have recently developed a theory of melting on essentially different lines. They attribute the main difference between solid and liquid to a change of order of the atoms, in analogy with the change of order which occurs in certain alloys. A similar suggestion was made independently about the same time by F. C. Frank[12] but was not worked out in a quantitative way. In order to get a model capable of mathematical treatment, Lennard-Jones and Devonshire considered a simple monatomic substance like argon, for which the forces were known. They had already calculated in some detail the equation of state of such a substance in an ordered arrangement at high densities. They then tried to improve this theory by considering how this state of order might break up as temperature and volume were changed. This would occur in a complicated way, but to simplify the picture it was assumed that atoms would ultimately begin to take up intermediate positions in the lattice. Thus if the original lattice is a face-centred cubic one, then a certain probability of occupation Q can be associated with each lattice site. The value $Q = 1$ corresponds to perfect order. But when Q becomes less than unity, there must be a finite probability of the atoms being elsewhere, and the question arises as to where they will go. It is assumed that the same probability Q can be associated with every lattice site. The remaining probability $(1-Q)$ must be attributed to all the other available positions within the lattice. Now the atoms on the lattice, distributed with density Q, set up a force-field and it can be shown that the potential energy has a stationary value at certain interstitial points. These are at the centres of the cubes whose faces contain the lattice points. They also constitute a face-centred lattice interpenetrating the first. The two together form a simple cubic lattice. It is assumed that the probability $(1-Q)$ can be associated with these points.

The energy difference between one of the original lattice points and these interstitial points will be a function of Q and of the dimensions of the lattice, that is of the volume. When $Q = \frac{1}{2}$ there is a state of perfect mixing and the assembly no longer has the properties of a solid. It is to be observed that this state of affairs, in which there are twice as many lattice points as atoms in simple cubic array, and each is occupied with a probability one half, is not the same as a solid with a simple cubic structure, for in one case there is interchange and in the other there is not. It is thus hardly correct to say that a state of disorder according to this theory is one in which portions of the crystal are in a simple cubic lattice and others in a face-centred lattice structure[13].

The problem of determining Q as a function of volume and temperature is somewhat similar to that occurring in the theory of alloys. The phenomenon is a co-operative one, and for each volume there is a definite temperature below which there is a certain degree of order (Q is between $\frac{1}{2}$ and 1) and above which there is complete disorder (Q is equal to $\frac{1}{2}$). The free energy of the system now

contains a new term corresponding to the state of order. For the same reason the pressure contains a new term. The equation of state is now quite different from that given in figure 3, which is the kind of result to be expected from any ordered assembly. It is shown in figure 4.

It is similar in type to that characteristic of evaporation and leads to a discontinuous change of volume at a certain temperature, dependent on pressure. While the volume is expanding during melting a state of disorder sweeps through the assembly. Thus for solid argon at the melting point, according to the theory, Q has a value of 0·95 which becomes 0·5 at the end of melting process.

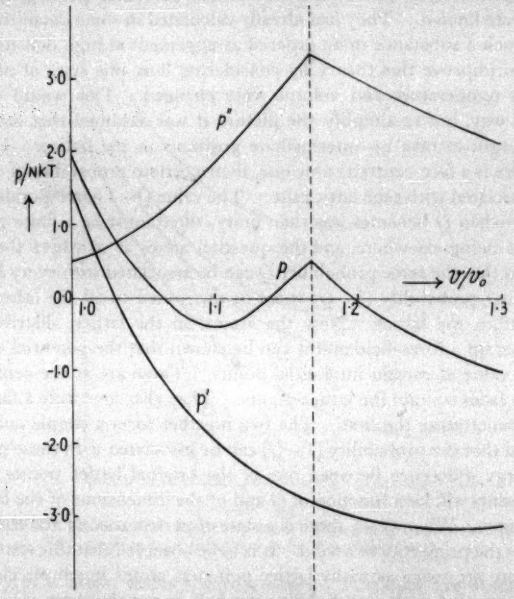

Figure 4. The equation of state of a solid showing the pressure due to the order-disorder transition.

The contribution of this change of order to the entropy of fusion is about 2 cal./deg., the total entropy change being 3·35 cal./deg. Thus it happens that in this case the calculated value of the order-disorder contribution is equal to k, the value appropriate to communal entropy, but this cannot be more than a coincidence. This method shows for the first time how a change of state from solid to liquid, or ordered array to disordered array, can occur, and how the temperature of melting can be related to pressure and interatomic forces.

O. K. Rice[13] has discussed the phenomenon of melting from the point of view of a change of coordination number. He suggests that this number should be considered as an additional parameter necessary to fix the properties of the system. For each value of the volume there would be one value of the coordination number for which the free energy would be a minimum. Thus in an ordered solid it would be 12 for a face-centred cubic and would change so that the average value became 11 or 10·5 or even less. A system with the value 11 could be regarded as a face-centred lattice in which every twelfth atom was removed, leaving a hole. This would give an energy just eleven-twelfths of the original arrangement, but it would correspond to a rather higher value of the volume per atom. A relation can be obtained in this way between energy and volume for known force fields. The calculation of the effect of coordination number on entropy is not so easy. If a hole is formed in a lattice, all the atoms round the hole have increased freedom of motion, but it is difficult to estimate the magnitude of the change. Rice has discussed in a general way what the effect is likely to be, but beyond giving reasons for values of the coordination number between 12 and 10, he is unable to formulate a quantitative treatment.

It has been suggested by Mott and Gurney[4] that a useful approach to the estimation of the entropy of a liquid may be to regard it as the limiting state of a polycrystalline solid in which the distinction between individual crystals has disappeared. The degree of order could be defined in some suitable way as a function of the average size of the crystals. The energy of the aggregate would contain a term dependent on the area of the surfaces of misfit and this could be expressed as a function of the degree of order.

In order to estimate the configurational entropy it is necessary to find the number of ways of putting the polycrystalline mass together with the same energy of misfit. A rough estimate can be obtained by assuming that, if any individual microcrystal be rotated about any axis, the number of positions which it can assume is of the same order as the number of atoms on any line drawn round its surface. This leads to a simple expression for entropy in terms of order. The free-energy curves plotted as a function of the degree of order change in type as the temperature rises, and there is one temperature for which the free energy of a single crystal and the polycrystalline arrangement can assume equal values and yet have a stationary value for small changes of the parameter representing order. This is described as the melting temperature. While this point of view is suggestive, it is difficult to see how it can be put on a quantitative basis in terms of force fields.

All these investigations represent different methods of approach to the problem of entropy in liquids and, while this problem cannot yet be regarded as solved, it seems likely that the changes which take place at melting will be found to be similar to those which occur in order-disorder transitions in alloys and other solids, though the process is obviously a more complicated one. An adequate theory should give the melting temperature in terms of pressure and make possible the calculation of heats of fusion.

§ 4. THE DISTRIBUTION FUNCTION

The other main theoretical problem which was referred to above was the determination of the average distribution of atoms in a liquid about any selected atom. One of the most promising lines of attack on this problem is by means of the x-ray diffraction patterns given by liquids. Since the early experiments of Debye and Scherrer[14] in 1916 great improvements have been made in technique and much valuable information has been obtained as to the variation of the intensity of the scattered radiation as a function of angle. Diffraction patterns were at first obtained for molecular liquids and the patterns were attributed to the interference of the x rays from atoms in the same molecule, but the examination of monatomic liquids such as argon has established the fact that patterns are produced by the units of which a liquid is composed as well as by the individual atoms in the same molecule. One characteristic feature of the patterns is that the scattering at small angles is small, whereas the scattering of x rays by gases leads to high intensities at small angles. An attempt to explain this difference in type led Debye to develop a theory of liquid scattering, and he was able to show that a probability distribution function could be inferred from observed intensity patterns. This function $\rho(r)$ was defined so as to give the probability that two atoms were at specified distances apart. It helps to define what Debye calls the quasi-crystalline structure of the liquid. It is not yet known whether this function corresponds to a unique distribution of matter in the liquid.

The form of this distribution function has now been found for a number of simple liquids. Menke[15] determined it for mercury and gallium and recently Gingrich[16] and his co-workers have dealt with sodium and potassium. The form of the function, expressed in terms of molecular size, is very much the same for these substances. An interesting method of simulating the distribution of atoms in liquids has been devised by W. E. Morrell[17], who constructed a model liquid with gelatin balls for molecules. This was found to give rise to a distribution function of the same type as that found for liquids from x-ray pictures.

If the distribution of atoms is homogeneous, the function $4\pi r^2\rho(r)$ gives the distribution of atoms about any other atom. This distribution may be regarded, following Prins[18], as made up of a series of coordination shells somewhat similar to those in a solid. The main difference to be expected is that these shells will not be at precise distances, but distributed with some degree of randomness about certain mean positions. The shape of these component distributions is not known but Prins assumed them to be like Gaussian probability curves.

A further development of this method has been made by Bernal[19]. Prins assumed the numbers N_i in the various coordination shells and the positions of their centres to be the same as in the solid, but Bernal takes them as parameters. Assuming that each shell is distributed according to a Gaussian probability function so that it is determined by N_i, r_i and a quantity λ_i which fixes the spread of the curve, he attempts to determine N_i, r_i and λ_i in terms of the values which these quantities have in the first coordination shell. By what he describes as

intuitive and semi-empirical methods he tries to solve the problem of distribution by examining the geometrical conditions which must be satisfied by successive shells, assuming that the assembly is molecularly homogeneous. By this is meant that there are no large fluctuations of density or large regions of crystal structure separated by others of completely gaseous disorder. The probability of finding a molecule at a given distance from another molecule is independent of the position of either of them in the liquid. By a consideration of possible geometrical arrangements, the quantities N_2, N_3..., as well as r_2/r_1, r_3/r_1..., are obtained, or rather shown to be obtainable, in terms of N_1. The distribution function is thus expressed in terms of three parameters only.

It is easy to calculate the energy of the assembly for given force-fields once the distribution function is given a definite form.* The problem of entropy is not so easy, and Bernal is unable to solve this aspect of the problem. He shows that the entropy will contain two important contributions, one due to the heat motion of the atoms and represented by a term of the type $N\log(h\nu/kT)$ and the other due to possible geometrical arrangements of the atoms. This is called the configurational entropy. It will depend on the spread of the distribution functions. Bernal assumes that it is proportional to the square of the quantity λ, which determines the spread. It is then possible to get a definite expression for the free energy and so to calculate the effect of configurational entropy on the specific heat at constant pressure, on the compressibility and other properties. It is suggested that there is a contribution to the specific heat from the changes in configuration, and this explains why the specific heat of liquids just above the melting point is higher than that of their solids.

Attempts have recently been made to calculate the shapes of the distribution curves for assumed models of liquids and given interatomic forces. Thus Walls [20] has considered a model in which each atom of a liquid is free to move in a spherical cell, the potential field being constant within this region and infinite outside it. This implies a uniform probability of finding the atom within equal elements of volume throughout the cell. It is then possible to calculate the probability that an atom in one cell is at a specified distance from one in another. This is a function of the size of the cells and the distance between their centres. Thus it is found that the probability of finding two specified atoms at a distance between r and $r+dr$ is

$$F(r)dr=(3r/5\sigma r_0)f\{(r-r_0)/\sigma\}dr, \qquad \ldots\ldots(16)$$

where σ is the radius of a cell and r_0 the distance between cell centres; the function f is given by

$$f(x)=1-\frac{5}{4}x^2\left\{1-\frac{1}{2}|x|+\frac{1}{40}|x|^3\right\}. \qquad \ldots\ldots(17)$$

If there are N_0 such atoms surrounding a central specified atom, then the probability distribution of these atoms is given by $N_0F(r)dr$. But this must equal

* Such calculations have recently been made by Hildebrand, Wakeham and Boyd [35] for liquid mercury.

$4\pi r^2\rho_0(r)dr$, where $\rho_0(r)$ is the probability function, as usually defined, of atoms in the first shell. Hence

$$4\pi r^2\rho_0(r) = N_0 F(r). \qquad \ldots\ldots(18)$$

Thus $\rho_0(r)$ contains three parameters N_0, σ and r_0. It is to be noted that $r\rho_0(r)$ is thus a symmetrical function of $|r - r_0|$.

A similar function is assumed for atoms which lie in other coordination shells outside the first, so that the composite density function is made up of a number of components appropriate to each shell, viz.

$$\rho(r) = \sum_i \rho_i(r). \qquad \ldots\ldots(19)$$

If a liquid is homogeneous, the three parameters just given should be sufficient to determine its structure, if with Bernal we suppose the number of atoms N_i in other shells and the distances r_i of the atomic centres can be determined in terms of N_0 and r_0. If the existence of such relationships be assumed, the remaining three parameters can be obtained by comparing the theoretical distribution with the one determined experimentally.*

An interesting application of these results can be made if σ can be expressed sufficiently accurately as a function of temperature. The free energy of the liquid is given for this model by equation (4), viz.

$$A = -N\boldsymbol{k}T\{\tfrac{3}{2}\log(2\pi m\boldsymbol{k}T/\boldsymbol{h}^2) + \log(\tfrac{4}{3}\pi\sigma^3)\} + \Phi, \qquad \ldots\ldots(20)$$

where Φ is the potential energy of the assembly. From this expression Wall estimates the value of the entropy at the melting and boiling points and infers a value for the entropy of fusion and vaporisation. This is a novel and suggestive application of X-ray results and is an interesting example of the correlation of experimental results, apparently unrelated, by an underlying theory.

The method used by Wall can easily be generalized to apply to any Einstein model of a liquid. Coulson and Rushbrooke[21] have shown that for all such models the theoretical distribution curve has the property that $r\rho_i(r)$ is symmetrical about r_i. Hitherto it has been assumed, as in Prins's assumption of Gaussian curves, that ρ itself was symmetrical. Hence any liquid which can be represented by an Einstein model should lead to a curve for $r\rho(r)$ which can be resolved into a series of peaks of similar shapes. It appears that the results for liquid sodium just above the melting point can be so interpreted, but the shapes of the individual peaks deviate somewhat from those derived for the simple model of spherical holes. The theory would have been improved had the atoms been treated not as rigid spheres but as having repulsive fields of a more suitable type. This calculation has been carried out by Lennard-Jones and Corner[22] for a liquid of argon atoms, whose force-fields are known, but in this case there is not as yet the experimental material available with which to test the results.

* It appears that the experimentally determined distribution for sodium, as provided by Trimble and Gingrich[16], can be reproduced in its main features by such a theoretical treatment, and values for N_0 and r_0 can be inferred. Thus for liquid sodium at 100° C, it is found that $\sigma = 0{\cdot}60$ A., $r_0 = 3{\cdot}79$ A. and $N_0 = 9{\cdot}28$ atoms.

A somewhat different approach to this problem has been made by J. G. Kirkwood[23], who has attempted to find a general relation which must be satisfied by the distribution function. First he obtains a relation between the probability of finding two specified molecules of a liquid at a definite distance apart, and the average work necessary to bring the molecules to that configuration from infinite separation in the liquid. This latter quantity $W(r)$ can be expressed as

$$W(r) = w(r) - w_0 + \chi(r), \qquad \ldots\ldots(21)$$

where $w(r)$ is the work required to create a cavity at the point r sufficient to contain a molecule (assumed to be a rigid sphere) and w_0 the work required to create a cavity at infinity, while $\chi(r)$ is the work expended in transferring one molecule from a cavity at infinity to a cavity at r. The quantity χ will depend on the nature of the attractive fields between the molecules. The relation which is obtained is equivalent to the statement that the probability function ρ is proportional to the product of $\exp(-\chi/\boldsymbol{k}T)$ and the probability of the existence of a cavity surrounding the point r.

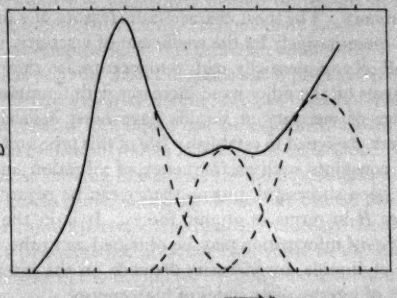

Figure 5. The distribution function of a liquid.

Now the probability that a cavity of given size is occupied can itself be expressed in terms of $\rho(r)$; it is, in fact, proportional to the integral of $\rho(r)$ over the volume of the cavity. It is then possible to infer the probability that the cavity is empty, that is, that a cavity exists. Thus $\rho(r)$ can be expressed in terms of an integral involving $\rho(r)$ over a volume of molecular size surrounding the point at the vector distance r. The result is that $\rho(r)$ must satisfy an integral equation of the type

$$\rho(r)\exp(\chi/\boldsymbol{k}T) = A\left[1 - \phi(r)\int_{\omega_0}\rho(r)dv\right], \qquad \ldots\ldots(22)$$

where A is a constant and $\phi(r)$ is a function which has to be introduced because of the possibility of more than one molecule (partly) occupying the volume w_0. It would be a constant if only one molecule at a time could occupy the hole of size ω_0. Each side of the above equation is equal to the ratio of the probability that a cavity of molecular size exists around the point r in the neighbourhood of a selected atom and the probability of a similar cavity at an infinite distance.

Kirkwood has succeeded in finding an approximate solution of the above equation under certain simple conditions, and the distribution function which he obtains does, in fact, reproduce the main features of those deduced from x-ray diffraction patterns. A typical example of such a distribution function is shown in figure 5.

Developments on these lines may be expected and more intimate understanding of liquid structure is likely to follow from the continued improvement of x-ray technique and the elaboration of theoretical methods of calculating distribution functions in terms of molecular forces. The kind of information which may emerge from such studies is the change in the number of immediate neighbours of any atoms as the temperature increases. Changes of coordination number may take place at melting and may be one of the essential features of the melting process.*

§ 5. OTHER LIQUID PROPERTIES OF THEORETICAL IMPORTANCE

There are other liquid properties which are likely to be of importance in the construction of a theory. The most characteristic feature of a liquid is its fluidity. This is expressed quantitatively by the coefficient of viscosity, which is found for most liquids to fall off exponentially with temperature, so that $\eta = A \exp(B/kT)$. The viscosity of gases on the other hand increases with temperature.

Simple theories of viscosity of liquids have been devised by Andrade[26], Eyring[27] and others, designed to establish a law of this type and to give A in terms of other physical constants such as frequency of vibration and so on. In this respect they have been successful, but no theory can be regarded as satisfactory unless it also gives B in terms of atomic forces. It is in the further study of viscosity that additional information may be obtained as to the energy associated with the disorder of liquids, for viscosity depends on the interchange of atoms and the attainment of intermediate states of high energy.

Secondly, it may be taken as certain that the theory and experimental study of *specific heats* will be valuable in the general development. There is no need to stress the importance of the theoretical treatment in the case of solids and gases, and it may be presumed that it will be equally significant in the case of liquids. On the experimental side it would be useful to have detailed measurements over wide ranges of temperature of simple liquids for which the forces are of a simple, known type.

The specific heats of liquid neon, argon[28] and mercury have been measured and show similar dependence on temperature, when plotted against a reduced

* Thus Miller and Lark-Horovitz [24] have recently reported that they have obtained diffraction patterns of liquid argon and have deduced that there are 10 neighbours in the first shell at a distance of 3·80 A. as compared with 12 at 3·82 A. in the solid. A concentration of next nearest neighbours is indicated at 5·4 A. and further concentrations at 6·7 A. and 7·9 A. Thus a comparison of the x-ray results from both liquids and solids may contribute to the solution of this difficult problem of the nature of the change of phase from solid to liquid. On the other hand Eisenstein and Gingrich [25], who also have obtained x-ray diffraction patterns of liquid argon, report a distribution of 7 atoms in the first shell at 3·90 A, and 5 atoms at about 5·05 A.

temperature. At the melting point C_v is rather higher than the asymptotic value characteristic of the solid (viz. 6 cal.). Reference has already been made to this and its probable explanation. The specific heat then decreases rapidly in the liquid range and has a value about 4 cal./deg. at the critical temperature. Beyond that there is a continuous fall to 3 cal. (gram. atom-degree), the value to be expected for a dilute gas.

It is tempting to attribute this, as Brillouin[9] has done, to a change in the character of the elastic waves. In a solid the Debye model leads to the concept of a set of longitudinal waves and another set, twice as numerous, of transverse waves. In the liquid the elastic constant associated with shear has disappeared and the transverse waves may be regarded as having lost their potential energy and as being replaced by a rotational motion. Under these circumstances they are equivalent to two degrees of freedom and not to four, so that their contribution to specific heat is k and not $2k$. The longitudinal waves, however, continue to contribute an amount k, and so the total specific heat is $2k$ or 4 cal./g. atom, as observed. This picture is suggestive, though too simple in its present form. A more elaborate treatment has recently been given by Lucas[29] in terms of elastic waves, and further developments in this direction seem likely.

Devonshire[30] has used the theory of solids and liquids given by Lennard-Jones and Devonshire[2, 11] to which reference has been made. He shows that the decrease of specific heat of the liquid can be explained as due to the changing type of field in which each atom moves as a result of expansion. It is not sufficient to regard the atoms as moving like simple harmonic oscillators, for the potential field in which the atoms move is not parabolic. It can be determined in terms of force-fields but is found to change in form as the volume of the assembly increases. The order-disorder phenomenon does not contribute to the specific heat in this theory because the disorder is complete. There can be no doubt, however, that the configurational entropy would contribute to the specific heat, and this is not adequately taken into account by the theory.

Space does not permit of an account of recent theories of evaporation (or rather of condensation). Important advances have recently been made in this subject, particularly by Mayer[31] and his collaborators, on the basis of classical statistical mechanics. The essential contribution which they have made is in the evaluation of the phase integral which occurs in the expression (2) for the partition function of a gaseous assembly. They have shown how to calculate this for a gas of increasing density by considering the interaction of the atoms in twos, threes and in clusters of greater complexity. An equation of state has thus been obtained which reproduces the main features of condensation. The process is not followed in detail to the liquid state, but what is obtained is the shape of an isotherm right up to the stage of condensation, and arguments are given for supposing that when the density reaches a certain value, further compression does not produce an increase of pressure but a condensation.

It is to be noted that the usual methods do not give such a result. Thus the

method of van der Waals leads to an approximate solution of the phase integral which is valid for small densities. It is then extrapolated to high densities where it is not valid. This well known equation of state gives an isothermal which is a *smooth* function of the volume. Below the critical temperature it is necessary to invoke special arguments such as the rule of constant areas to derive the pressure of the saturated vapour. This isotherm is not therefore derived from the phase integral.

The Mayer theory of condensation does not, however, in its present form throw any light on the nature of liquid structure, for the process of condensation is not followed in detail.

Lennard-Jones and Devonshire[2),(11)] have used their model of a liquid to calculate the changes produced on evaporation, and by the usual thermodynamic methods have derived equations which determine the boiling temperature as a function of pressure. The heat of evaporation is then evaluated in terms of the constants of the force-field. Other calculations of a similar kind, though not based on force-fields of such a general type, have been given by Eyring[32] and collaborators.

A theory of evaporation has been given by Cernuschi and Eyring[33] based upon a model fluid in which the liquid and vapour phases are treated as alloys of holes and molecules. This leads to precise conditions for a critical temperature in terms of the energy of interaction of the atoms but, as Kirkwood[33] has pointed out, the theory predicts critical temperatures several times larger than those observed. This is due to the failure of the theory to take into account in a satisfactory way the effect of holes on the lattice vibrations and their contribution to the free energy.

§ 6. CONCLUSION

The general conclusion at which we arrive as a result of this review of the present state of knowledge of liquid structure is that the fundamental problem is the determination of entropy. While recent investigations may not have succeeded in solving this difficult problem completely, they have at any rate produced physical pictures which are instructive. Whether we regard liquids as alloys of holes and atoms or as assemblies of infinitely variable geometrical configuration is not important so long as we can find a model which will permit of the correlation of those liquid properties which are known and the prediction of other properties which are still unknown.

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THE VISCOSITY OF LIQUIDS*

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§ 1. INTRODUCTION

The chief matters which I wish to discuss briefly are (1) the viscosity of liquids at the melting point, (2) the effect of an electric field on the viscosity of liquids.

An estimate of the viscosity from other physical data, such as can be found in tables, has always seemed to me to be a desirable feature of any theory of liquid viscosity, and, as far as I know, the more complicated theories, based upon considerations of partition functions, have failed not only to provide such an estimate, but have in general involved undetermined parameters in such a way that any experimental verification is difficult, except in the matter of generalities. Any explanation of viscosity by ordinary diffusion processes, by migration of one atom or molecule bodily from one layer to another, in the way considered in explaining the viscosity of gases, appears to me to be unsatisfactory, in view of the measurement of the coefficient of self-diffusion of molten lead, which, as I have shown [1], would on this basis lead to an estimate of viscosity far too small. The attempts of chemists to deduce regularities for the boiling-point viscosity would appear to be very artificial, since the boiling point is grossly dependent upon the purely arbitrary pressure considered. The experiments of Bridgman have shown that viscosity is not a function of volume only, as many workers assumed before viscosities at different temperatures but constant volume were available. These are general points which need to be considered in attempting anything towards a theory of viscosity.

The effect of an electric field on the viscosity of liquids has some bearing on the value of c in the formula $\eta = Ae^{c/T}$, to which Professor Lennard-Jones has referred. We can estimate the change of energy of a molecule in the given applied field and see how it compares with the energy factor, c. This will give a rough indication as to the magnitude of the effect to be expected.

Considering melting-point viscosity, some time ago [1] I put forward a simple theory of liquid viscosity, based on an interchange of momentum between molecules in adjacent layers. The mean position of each molecule was assumed not to change appreciably during the time of one vibration, and communication of momentum was assumed to take place at each extreme libration when the liquid was just at the melting point. This led to a formula for η_M, the melting-point viscosity, in terms of the molecular weight A, the absolute temperature of melting T_M and the density ρ, viz.,

$$\eta_M = 5{\cdot}1 \times 10^{-4} (AT_M)^{1/2} / V^{2/3},$$

* A contribution to the discussion on the Liquid State.

where $V=A/\rho$ is the molecular volume at the melting point. The constant $5{\cdot}1\times10^{-4}$ is not arbitrary, but is $\frac{4}{3}\frac{C}{N^{2/3}}$, where C is the constant in Lindemann's melting-point formula, N is Avogadro's number, and $\kappa=4/3$ is a constant which must be somewhere in the neighbourhood of 1. κ has its analogy in the constant k in the familiar formula for the viscosity of a gas:

$$\eta=k\rho\bar{u}\lambda.$$

In the gaseous case, from rough calculations, $k=1/3$: more refined calculation gives, for spherical molecules, $k=0{\cdot}499$; for any ordinary type of molecule k cannot be very far from unity, but has not been calculated precisely except for the simplest molecules, and then with great difficulty. Similar considerations hold for κ in the liquid case. There is little likelihood that it can be calculated in the present state of the theory of the liquid state, but it must be about unity.

This suggests that it is better, perhaps, to write the formula for liquid viscosity at the melting point as

$$\eta_M=K(AT_M)^{1/2}/V^{2/3},$$

where K cannot be far from 5×10^{-4}, and to seek the exact value of K from experiment, as long as it is remembered that a rough value of K is given, in the simplest case of monatomic molecules, by general considerations, and that with this rough value the calculated viscosities lie close to the experimental values. The theory does predict melting-point viscosities for monatomic liquids, independent of any exact calculation of κ.

§ 2. PARTICULAR TYPES OF LIQUID

I propose to consider, in addition to monatomic liquids, a few simple classes of liquids, to see how far a fixed value of κ can be attributed to each class and to consider the implications of the experimental results.

(a) *Monatomic liquids*

Besides the data for monatomic liquids used in my original paper[1], there are now available experimental figures for liquid sodium, potassium[2] and caesium,* from work done in my laboratory, and for argon[3]. In the following table, η,

Table 1

Substance	Atomic weight	Melting point (° K.)	$\eta\times10^3$	ρ	α	$\beta\times10^4$	$\eta\times10^3$ (calc.)	$\frac{\eta_e-\eta_c}{\eta_e}\times100$
Argon	39·9	84	2·82	1·42	6·26	4·51	3·47	−23
Potassium	39·1	335·5	5·37	0·830	8·75	6·13	4·85	+ 9
Caesium	132·8	301·4	6·09	1·839	11·54	5·28	6·40	− 5
Sodium	23·0	370·6	6·95	0·929	10·86	6·39	6·06	+13
Tin	118·7	505	19·7	6·97	37·0	5·33	20·5	− 4
Mercury	200·6	234·2	20·4	13·69	36·2	5·63	20·1	+ 1
Lead	207·2	600	29·8	10·65	48·7	6·12	27·1	+ 9
Copper	63·6	1356	38	8·2	75·0	5·06	41·6	− 9

* Unpublished.

the coefficient of viscosity, and ρ, the density, both refer to the melting point: α is the value of $(AT_M)^{1/2}/V^{2/3}$: $\beta = \eta/\alpha$. The melting point is given on the absolute scale.

The value of η_c is that calculated with the average value of β, which is $5{\cdot}56 \times 10^{-4}$. The theoretical value of β is $\kappa CN^{-2/3}$, where κ is the numerical constant which was taken as 4/3 in the original paper. Taking C as $2{\cdot}8 \times 10^{12}$ and N as $6{\cdot}06 \times 10^{23}$ we have $\kappa = 1{\cdot}42$, in place of the 1·33 originally assumed, so that

$$\eta = 1{\cdot}42C\,(AT)^{1/2}/(NV)^{2/3}.$$

All the substances in the table, except mercury and tin, crystallize in the cubic form. Mercury is rhombohedral, not badly distorted from cubic form. Tin is tetragonal body-centred. It will be seen that the range of viscosity is from $2{\cdot}8 \times 10^{-3}$ to 38×10^{-3}, namely, in the ratio of 1 to 14, and the other constants involved cover a wide range. The worst discrepancies are argon and sodium, with errors of 23 and 13 per cent respectively. The other discrepancies are within 10 per cent.

The remaining metals for which data are available are antimony, bismuth and gallium, which are well known to be of complex crystalline structures, and so do not invalidate the simple theory, as was pointed out in my original paper. The values of β for these three metals are 3·10, 4·04 and 7·13 respectively. These metals are always exceptional as compared with those in table 1: for instance, the ratio of electrical resistance of solid to that of liquid is about 0·5 as compared to values in the neighbourhood of 2 for the other metals cited.*

(b) *Fused salts of cubic structure*

In fused salts of the NaCl type the atoms (ions) of the two different elements are not bound together as diatomic molecules, but have what is practically a separate existence, no metal atom being more bound to any one of its nearest neighbours than to any other one. Hence we may expect such salts to behave, as a first approximation, as monatomic liquids in which the molecular weight is the mean of that of the two constituent elements.

As regards fused salts of halides showing simple cubic structure, we have the values of R. Lorenz [4] for NaCl, NaBr, KCl and KBr and the values of Dantuma [5] for NaCl. The values of Lorenz and his collaborator are very rough ("Es sei hier betont, dass diese Werte auf grosse Genauigkeit keinen Anspruch machen"): those of Dantuma seem more precise, and give an approximately linear plot for log η against $1/T$, which is always a good test with simple liquids. For NaCl three of Lorenz's values lie within 3 per cent of those of Dantuma at the same temperature: the fourth is about 6 per cent out. For viscosities this is not bad agreement, but whereas Dantuma's values,

* See Mott and Jones, *Properties of Metals and Alloys*, p. 278.

being regular and extending nearly to the melting point, permit a good extrapolation to the melting-point value, those from Lorenz's laboratory, which are less regular and do not, in general, approach the melting point, give a less reliable value.

The melting points of some of these halides, particularly NaBr, are the subject of some discrepancies. I have endeavoured to make a decision as to the best values; to discuss the matter in detail would take too much space.

Table 2. Fused halides of alkali metals

Substance	Average atomic weight	Melting point (° K.)	$\eta \times 10^3$	ρ	α	$\beta \times 10^4$
NaCl	29·2	1077	1·59	1·54	25·0	6·36
NaBr	51·5	1013	1·63	2·34	29·1	5·61
KCl	37·2	1049	1·50	1·52	23·4	6·41
KBr	59·5	1013	1·52	2·11	26·5	5·74

These give an average value for β of $6{\cdot}03 \times 10^{-4}$, as compared with 5·56 for the elements in table 1. The difference of 8 per cent does not exceed probable experimental errors, considering the uncertainty as to the exact value of the viscosities, and even the melting points. Fused halides of the alkali metals can be considered, then, as if belonging to the class of monatomic liquids.

(c) *Molecules of high symmetry*

Possibly after monatomic molecules the next simplest type, from the point of view of viscosity, should be molecules with approximately central symmetry. The data are unfortunately scanty. Determinations for SnI_4, $SnBr_4$, $SiCl_4$ and other similar liquids were about to be undertaken in my laboratory when war compelled the abandonment of the investigation.

There are available, however, accurate figures for CCl_4 and liquid CH_4 [10]. A few determinations have been made for $SiCl_4$ [6], between 0° and 35, from which we have to extrapolate to $-89°$ c. to get the melting-point viscosity, so that the result is probably not very accurate. For $SnCl_4$ the data are very unsatisfactory, and for $TiCl_4$ only two determinations are accessible, much too close together for extrapolation.

The results are expressed in the following table :—

Table 3

Substance	Atomic weight	Melting point (° K.)	$\eta \times 10^3$	ρ	α	$\beta \times 10^4$
CH_4	16·0	89	2·26	0·466	1·122	20·1
CCl_4	153·8	250	19·8	1·68	9·64	20·5
$SiCl_4$	170·1	184	15·3	1·73	8·30	18·5

The agreement between CH_4 and CCl_4 is astonishing, considering that the viscosities here are as 1 to 9, and shows that there can be no rotational element in the viscosity, since for CH_4 the mass is concentrated near the centre, and for CCl_4 near the outside. The degree of disagreement for $SiCl_4$ (less than 8 per cent) is without significance in view of the long extrapolation required to get the melting-point viscosity.

Molecules of less high symmetry, but still good symmetry about one axis, are $CHBr_3$ and $CHCl_3$, for which data are available.

Table 4

Substance	Atomic weight	Melting point (° K.)	$\eta \times 10^3$	ρ	α	$\beta \times 10^4$
$CHCl_3$	119·3	209·5	18·1	1·64	9·08	19·9
$CHBr_3$	252·7	280·7	25·2	2·90	13·5	18·7

The values of β agree within 6 per cent or so, with an average of 19·3, which is a little lower than for the CH_4 class.

(d) *The halogens*

Table 5 gives the values for the available halogens. There is some discrepancy concerning the value for bromine. That given in the table is due to Steacie and Johnson[7], which agrees pretty well with that of Thorpe and Rodger. However, Beck[8], whose value for iodine agrees well with that of Steacie and Johnson, finds a value of $\eta_M = 0{\cdot}0145$ for bromine at the melting point, which gives $\beta = 9{\cdot}6$. Kann[9] finds a still higher value, about 15 per cent in excess of that of Steacie and Johnson, which makes the value of β for bromine agree exactly with that for chlorine, but it does not seem at all likely that Kann's value is correct.

Table 5

Substance	Molecular weight	Melting point (° K.)	$\eta \times 10^3$	ρ	α	β
Cl_2	70·9	172·2	10·05	1·719	9·24	10·9
Br_2	159·8	265·9	13·7	3·21	15·2	9·0
I_2	253·8	386·6	23·1	3·98	22·0	10·5

It will be seen that the agreement for Cl_2 and I_2 is good, while the value for Br_2 is somewhat low if what appears to be the best value for η is taken.

It may be added that for the two molecules N_2 and CO the values of β are 7·52 and 7·81 respectively, but this agreement is not very significant, since all the physical properties of the molecules are so similar.

(e) *Molecules which depart greatly from central symmetry*

Lest it be thought that, by some chance, this kind of agreement occurs irrespective of the shape of the molecule, we may take the phenyl halides, where the asymmetry increases as we go from F to I.

Table 6

Substance	Atomic weight	Melting point (°K.)	$\eta \times 10^3$	ρ	α	β
C_6H_6	78	278·4	8·17	·893	7·48	10·9
C_6H_5F	96	231·8	15·1	1·09	7·54	20·0
C_6H_5Cl	112·5	227·8	23·3	1·175	7·65	30·5
C_6H_5Br	156·9	242·4	27·2	1·56	9·03	30·1
C_6H_5I	204·0	241·6	44·6	1·91	9·86	45·3

Here we have a great increase, of over 1 to 4, from benzene to iodobenzene.

Another striking case is offered by the paraffins. The value for liquid methane[10] is probably reliable. The extrapolations necessary to get the melting-point viscosities for hexane, heptane and octane from the published data are so distant that they have not been considered. The measurements for decane and undecane are due to Bingham and Fornwalt[11].

Table 7

Substance	Atomic weight	Melting point (°K.)	$\eta \times 10^3$	ρ	α	β
CH_4	16·0	89	2·26	0·466	1·122	20·1
C_8H_{18}	114·1	216·4	20·2	·775	5·59	36·2
$C_{10}H_{22}$	142·2	241	23·9	·769	5·70	41·9
$C_{11}H_{24}$	156·2	246·5	29·3	·776	5·71	51·3

Here we see a rapid increase of β with increasing length of molecule. This is what we should expect, for here the stick-like molecules must actually get in one another's way, and so exchange momentum by a mechanism not considered in the theory.

§ 3. CORRECTIONS TO THE FREQUENCY FORMULA

Lindemann's theory is based upon Einstein's formula for the frequency of vibration of an individual atom in a regular array, which implicitly assumes a single frequency ν. Lindemann assumes a simple harmonic vibration characterized by $m\frac{d^2x}{dt^2} = -\alpha x$, $\nu = \frac{1}{2\pi}\sqrt{\left(\frac{\alpha}{m}\right)}$, which gives a maximum kinetic energy

$$\tfrac{1}{2}\alpha A^2 = \frac{h\nu}{e^{h\nu/kT_M} - 1},$$

where A is the amplitude of the vibration. He further assumes that melting takes place when the amplitude of vibration attains a value $\frac{1}{2}s\sigma$, where σ is the

distance between centres of atoms in their equilibrium positions, supposed to be in cubical array, and $s\sigma$ is the distance between the peripheries of the atoms in their equilibrium positions. Then

$$\nu^2 = \frac{2}{\pi^2 s^2 \sigma^2 m} \frac{h\nu}{e^{h\nu/kT_M} - 1}. \qquad \ldots\ldots(1)$$

To simplify this, Lindemann takes $h\nu/kT_M$ small, so that

$$\nu^2 = \frac{2}{\pi^2 s^2 \sigma^2 m}(kT_M - \tfrac{1}{2}h\nu). \qquad \ldots\ldots(2)$$

This gives
$$\nu = BT^{1/2} - \frac{1}{4}\frac{h}{k}B^2 + \frac{1}{32}\frac{B^3 h^2}{k^2}T^{1/2}, \qquad \ldots\ldots(3)$$

where
$$B = \frac{1}{\pi s \sigma}\sqrt{\frac{2R}{A}}.$$

A is the molecular weight and R is the gas constant. As a first approximation,

$$\begin{aligned}\nu &= BT^{1/2} \\ &= \frac{\sqrt{2B}}{\pi} s^{-1} N^{1/3}\left(\frac{T\rho^{2/3}}{A^{5/3}}\right)^{1/2} \\ &= C(T/AV^{2/3})^{1/2},\end{aligned}$$

where V is the atomic volume. The value of s being unknown, Lindemann found C by comparison with the best values for ν found by other methods for certain bodies.

Two approximations have been made for which corrections can be applied. The correction due to neglect of the second term in (3) is

$$\frac{1}{4}\frac{h}{k}BT^{1/2} \times 100 \text{ per cent.}$$

The value of h/k being about $4{\cdot}78 \times 10^{-11}$, this correction amounts to $1{\cdot}195 \times 10^{-9} BT^{1/2}$ per cent. The third term in (3) is smaller and only comes into account if T is small (only in the case of argon among the substances of table 1 is it in excess of 1 per cent). The other approximation is made in taking $T - \frac{\beta\nu}{2}$ for $\left(\frac{\beta\nu}{e^{\beta\nu/T} - 1}\right)^{1/2}$, where $\beta = h/k$. Knowing ν to a first approximation, the error due to this can be estimated.

There is, however, a third assumption made in Lindemann's work which is only roughly true, namely, that s is the same for all elements, or, in other words, that Grüneisen's rule is true, which states that for all simple solids the increase in volume from absolute zero to melting point is about the same fraction of the volume, viz. 7·5 per cent. It is possible in certain cases, where the necessary data are available, to calculate the volume at absolute zero and to find the actual increase of volume to the melting point, from which relative values of s can be found. It is of interest to note, in view of the many attempts to bring the " free volume " into considerations of viscosity, that Lindemann's formula involves s,

which is a measure of the free volume, so that our melting-point viscosity formula does involve this quantity. I have applied corrections for the approximations mentioned in the case of some monatomic liquids where the data are available. There is some slight increase in regularity, especially in the way of bringing the value of β for argon closer to the other values, but as the results are incomplete and time is lacking for a proper discussion, I do not wish to do more than refer to the matter.

What I would put before you, then, is the suggestion that the value of $\beta = \frac{\eta_M V^{2/3}}{(AT_M)^{1/2}}$ is approximately constant for molecules of a given characteristic shape. The value of β is, it should be noted, least for monatomic liquids, in which we include fused salts such as NaCl, and has a value only slightly greater for N_2 and CO, which, on the Langmuir type of model, is to be expected. Long rod-like molecules have a high value of β, which again is to be expected, since with such molecules there must be communication of momentum by actual "entanglement", part of one molecule being at all times in the way of another, for laminar motion. As regards the comparatively high value of β for molecules of the CCl_4 type, while these have a high degree of central symmetry the field is far from being spherically uniform, so that the fields of adjacent molecules interpenetrate far more than is the case with truly spherical (monatomic) molecules. It is possible that β will prove a useful index in considering liquid structure.

§4. EFFECT OF ELECTRIC FIELD ON VISCOSITY

Turning to the problem of the effect of an electric field on viscosity, this question has been the subject of a large amount of discordant work. Dr. Cyril Dodd and I have carried out an extensive investigation, publication of which has been delayed by the war, which also prevented us from obtaining final results in some directions. We think, however, that we have cleared up the causes of the discrepancies found with polar liquids, and it may be of interest to indicate briefly our results. In these experiments the flow took place through a horizontal channel of rectangular cross-section, of which the height (0·2 to 0·28 mm.) was very small compared with the width (1 cm.), the difference of potential being applied to the two insulated horizontal metal plates bounding the channel.

As regards non-polar liquids, such as benzene and carbon disulphide, it seems generally agreed by more recent workers[12],[13],[14] that there is no effect. We have confirmed this with somewhat higher fields and greater accuracy than previous workers, and can say that with an apparent field (the phrase will be explained later) of 40 kilovolt/cm. transverse to the flow there is no change in the viscosity exceeding 1 part in 6000. Theoretical considerations of energy do not lead us to expect an effect of this magnitude.

We find that polar liquids fall into two classes—(I) those showing no effect, which include ether, monochlorbenzene, toluene, anisole and meta-xylene, all in a dry state; and (II) those showing an effect, in general a very large effect. These

include aceto-nitrile, acetone, dimethylamine, ethylene dichloride, *n*-propyl chloride and alkyl acetates. Liquids of class I have an extremely low conductivity, liquids of class II have a much higher conductivity under the conditions of the experiment. Wet ether and wet monochlorbenzene have a conductivity of the higher order and show an effect, but conductivity as such is not the determining condition, for wet CCl_4 and benzene conduct, but show no viscosity effect.

The type of variation of the viscosity effect with field for liquids of class II is shown in figure 1. The viscosity increases slowly at first, then rapidly, and

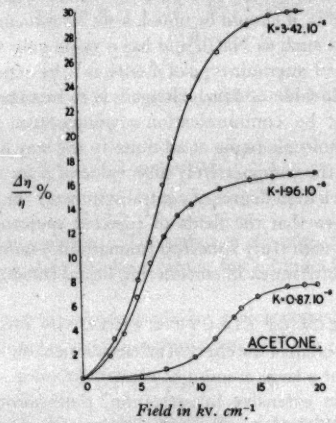

Figure 1.

finally reaches a saturation value which may be from 10 to 100 per cent above the normal value[15]. This saturation value may be taken as an index of the magnitude of the effect. We found, by subjecting liquids such as aceto-nitrile and acetone to successive processes of repeated distillation in the presence of phosphorus pentoxide, that we could reduce the conductivity K, and that this reduction was accompanied by a proportional reduction of the viscosity effect, the results indicating that there would be no effect, or an extremely small effect, at zero conductivity. In figure 1, results for acetone of three different conductivities are shown.

Three other lines of experiment helped to elucidate the problem, dealing respectively with the effect of alternating fields of various frequencies; the effect of a field along the direction of flow, for which a special apparatus was designed; and the effect of the height of the channel, that is, of the distance between the plates to which the difference of potential is applied. With alternating fields of low frequency, in the region of 100 cycles/sec., the effect is the statical one, averaged over the cycle, but as the frequency is increased a point is reached (at

about 400 cycles/sec. with a 0·20 mm. gap) where the effect begins to diminish, and at frequencies of some 2000 cycles/sec. the effect has practically disappeared. With the longitudinal field, produced by applying potentials of some 80,000 volts between plates 6 cm. apart, there is no effect even with a liquid which shows an effect of 25 per cent for the same apparent field when applied transversely. With increasing distance between the boundaries of the channel used as electrodes the effect diminishes, and calculation shows that the observed results could be produced by an immobile layer, of constant thickness, at the surface of the plates, the effect of which would, of course, be less marked for wide gaps than for small.

All these results go to show that with conducting polar liquids a layer of immobile molecules is built up at each plate. If the field alternates so rapidly that ions have not time to be driven across the gap the effect will be diminished, and consideration of the frequency at which the effect begins to decrease gives a mobility of the ions in good accord with that to be anticipated. In the apparatus used for the longitudinal effect there is no tendency for ions to be driven on to the walls of the narrow channels through which the liquid flows.

If we now examine the two classes of polar liquids we see that with ordinary dry liquids of class I there is no tendency to ionization, while liquids of class II are all capable of ready ionization through combination with small traces of water. Thus aceto-nitrile, $CH_3.C{\equiv}N$, with H_2O probably goes to $(CH_3.CNH)^+$ and OH^-, and similar effects take place with acetone, di-methylamine and esters. For ethylene chloride and *n*-propyl chloride the ions responsible for the conductivity may be supposed to be H_3O^+ and Cl^-, formed by hydrolysis of the chloro-hydrocarbon. The ions form space charges in the neighbourhood of the electrodes, and, owing to the non-uniform field within the region of these charges, the polar molecules are strongly bound to the plates and form an immobile layer, the thickness of which is estimated at 0·0085 mm. for chloroform and of the same order for other liquids.

As regards ether and monochlorbenzene saturated with water, wet ether is capable of ionization according to the scheme $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!\overset{+}{O}H \mid \overset{-}{O}H$, while with wet monochlorbenzene, which shows a comparatively small viscosity increase, the conduction and viscosity changes may be due to the water alone.

A consequence of the formation of space charges at the electrodes, with abnormal cathode and anode fall, is that the field in the body of the liquid will be markedly less than what I have called the "apparent" field, namely the applied difference of potential divided by the separation of the electrodes. Strong confirmation of this is afforded by the fact that the conductivity of such liquids as aceto-nitrile and acetone, measured in a conductivity apparatus with alternating current, came out to be much greater than that obtained from the current passed in the viscosity apparatus and the voltage applied to the electrodes. In the case of aceto-nitrile, for instance, it was about 60 times as large. This indicates that

the effective potential, applied to the region of the liquid where there is no space charge, is very much less than that calculated on the assumption of a uniform field.

Even in the cases where the conductivity is small and there is no viscosity effect, there may be abnormal falls of potential in very narrow regions, near the electrodes, so that the apparent field may be much greater than the real field. It may be recalled that even in a highly exhausted space Aston found that the applied difference of potential did not accurately give the field existing in the space between the electrodes.

It would appear, then, that the true viscosity effect should be sought with alternating fields sufficiently high to avoid space charges at the electrodes and sufficiently low to avoid effects due to the relaxation time. Fortunately this gives a wide possible range. As soon as conditions admit, such experiments will be undertaken. Meanwhile our work indicates that all of the conflicting data as to the effect of an electric field on the viscosity of polar liquids should be treated with great caution.

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RELATIONS BETWEEN THERMO-PHYSICAL PROPERTIES *

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THE main object of these remarks is rather to propound problems than to make attempts to solve them—to draw attention to a few remarkably simple relations which hold, with considerable accuracy, over the whole range of existence of certain liquids, from freezing point to critical temperature. Most of the attempts made to calculate values of the constants involved in such relations in terms of modern theory are confined to estimates made in the neighbourhood of a definite point in the temperature-history of the liquid—the critical point, for example. (A notable exception to this statement is Andrade's explanation of the relation between viscosity and temperature.) And it must be emphasized that it is of the essence of the relations collected here that they are *not* short-range formulae which will not bear extrapolation—not, as it were, tangents to, or sectors of, a curve—but hold, as has been said, with high approximation, over the whole range of the liquid's existence. It is further to be borne in mind that the formulae are valid only for liquids which are unassociated, or for those liquids whose degree of association is unaffected by changes in temperature; and that, although there is a very significant clustering of the values of some of the constants round certain simple numbers, if a high degree of accuracy of computation of any particular property is demanded, the values of the constants appertaining to the liquid under consideration must be chosen.

One of the more fundamental of these formulae is that which gives the relation between surface tension (γ) and temperature. This, which was put forward by van der Waals in 1894 [1], may be written

$$\gamma = \gamma_0(1-m)^n, \qquad \ldots\ldots(1)$$

where m stands for reduced temperature, and n is very approximately the same for all (unassociated) liquids, having a value about 1·2. Van der Waals gave reasons to show that

$$\gamma_0 = K\theta_c . V_c^{-2/3}, \qquad \ldots\ldots(2)$$

where θ_c stands for the critical temperature and V_c for the critical molecular volume. The investigation passed practically unnoticed, and I chanced upon the formula independently about twenty years later [2] while looking for a method of

* A contribution to the discussion on the Liquid State.

deducing, with some accuracy, critical temperatures from observations of surface tension made over a limited range of temperature. It was noticed that a plot of $\gamma \div \delta\gamma/\delta t$ against t was very accurately linear, leading at once to

$$\gamma = \gamma_0'(1-bt)^n, \qquad \ldots\ldots(3)$$

where b is the reciprocal of the critical temperature. The closeness with which $1/b$ approximates to t_c (t is here reckoned in degrees Centigrade) and the variations in the value of n are shown in table 1.

Table 1. Values of b and n in $\gamma = \gamma_0'(1-bt)^n$

Substance	n	b	$t_c = \frac{1}{b}$	t_c obs.	Diff.
			°	°	°
Ether	1·248	·005155	194	193·8	+0·2
Benzene	1·218	·003472	288	288·5	−0·5
Chloro-benzene	1·203	·002793	358	359·2	−1·2
Carbon tetrachloride	1·206	·003553	281·5	283·1	−1·6
Methyl formate	1·210	·004695	213	214·0	−1·0
Methyl acetate	1·200	·004274	234	233·7	+0·3
Methyl propionate	1·202	·003891	257	257·4	−0·4
Methyl butyrate	1·195	·003559	281	281·3	−0·3
Methyl iso-butyrate	1·228	·003731	268	267·6	+0·4
Ethyl formate	1·187	·004255	235	235·3	−0·3
Ethyl acetate	1·217	·003984	251	250·1	+0·9
Ethyl propionate	1·192	·003663	273	272·9	+0·1
Propyl formate	1·231	·003774	265	264·9	+0·1
Propyl acetate	1·204	·003623	276	276·2	−0·2

Mean value of $n = 1{\cdot}210$.

Another equation of fundamental importance was discovered by Macleod[3] in 1923. This is

$$\gamma/(\rho_l - \rho_v)^p = C, \qquad \ldots\ldots(4)$$

where C is a constant independent of the temperature, and p was taken by Macleod as equal to 4. Here again, if a high order of accuracy is demanded, it is necessary to take into account individual deviations of p from the rough value 4. The point is worth noticing when making calculations of the parachor P ($= MC^{1/p}$, where M is the chemical molecular weight of the substance considered). Table 2 shows the effect on the parachor of deviations from the value 4.

Table 2

Substance	p	$\frac{M\gamma^{1/4}}{\rho_l - \rho_v}$	$\frac{M\gamma^{1/p}}{\rho_l - \rho_v}$
Benzene	3·91	205·9	209·9
Chloro-benzene	3·95	243·6	246·3
Ether	4·12	211·6	207·3
Methyl formate	3·98	138·0	138·7
Ethyl acetate	3·94	217·5	219·8

The relation between *free* surface energy (γ) and *total* surface energy (λ) is given by

$$\lambda = \gamma - m\partial\gamma/\partial m. \qquad \ldots\ldots(5)$$

Hence, if the relation between γ and temperature is given by equation (1), the march of λ with temperature is

$$\lambda = \gamma_0(1-m)^{n-1}.[1+m(n-1)], \qquad \ldots\ldots(6)$$

or

$$\lambda = \gamma_0(1-m)^{0\cdot2}(1+0\cdot2m), \qquad \ldots\ldots(7)$$

if we take $n = 1\cdot2$ for all substances.

If, following Katayama[4], we define free molecular surface energy (e) and total molecular surface energy (E) by the equations

$$e = \gamma[M/(\rho_l - \rho_v)]^{2/3} \text{ and } E = \lambda[M/(\rho_l - \rho_v)]^{2/3}$$

instead of the more usual forms in which ρ_v is omitted, we easily see, on substituting from (1) and (4), that

$$e = e_0(1-m)^{n-2n/3p} \qquad \ldots\ldots(8)$$

and

$$E = E_0(1-m)^{n-1-2n/3p}[1+m(n-1)], \qquad \ldots\ldots(9)$$

with $E_0 = e_0$.

If we put $n = 1\cdot2$, $p = 4$, these equations take on the simple form

$$e = e_0(1-m)\ ;\ E = E_0(1+0\cdot2m).$$

It is hardly likely that E will increase with m in linear fashion up to the limit $m = 1$. Reference to the experimental values of n and p and to equation (9) shows that in every instance examined $n-1-2n/3p$ is a small positive fraction, so that E vanishes when $m = 1$.

Some little time ago[5], Mr. Kennedy and I calculated and tabulated values of γ_0, n, p, and e_0 for some forty pure organic liquids. This table, used in combination with the principal equations just quoted, enables one to follow in detail the main surface properties of the liquids studied.

In this paper we have also attempted to work out from the experimental figures values of γ_0, e_0 and P in terms of the critical constants where these are available. Putting

$$\gamma_0 = K\theta_c^{\alpha}V_c^{\beta}$$

we find that

$$\gamma_0 = 3\cdot12.\theta_c.V_c^{-0\cdot55}. \qquad \ldots\ldots(10)$$

(Compare with van der Waals' deduction $\gamma_0 = K\theta_c V_c^{-0\cdot67}$.)

Similarly,

$$e_0 = 0\cdot811\theta_c V_c^{0\cdot176} \qquad \ldots\ldots(11)$$

and

$$P = 0\cdot324\theta_c^{1/4}V_c^{7/8}. \qquad \ldots\ldots(12)^*$$

* There is a possible misprint in one of the indices of V_c which I cannot at the moment trace. Putting $p = 4$ and $n = 1\cdot2$ we have $e_0 = \gamma_0^{5/8}P^{2/3}$. With the indices given for e_0 and γ_0 this leads to $P = A\theta_c^{1/4}V_c$ in round numbers. My recollection is that we worked out the values of the indices independently in each instance.

Mr. Corner, in a communication to this discussion, has noted that, from simple dimensional considerations, we have

$$P = K_1\theta_c^{1/4}V_c^{5/6}.$$

If we apply these considerations to γ_0 and e_0 we find

$$\gamma_0 = K_2\theta_c V_c^{-2/3} \text{ and } e_0 = K_3\theta_c V_c^{0}.$$

If we eliminate γ between equations (1) and (4) we at once have

$$\rho_l - \rho_v = \rho_0(1-m)^{0\cdot3} \qquad \ldots\ldots(13)$$

if we take $n = 1\cdot2$, $p = 4$. This equation, if we drop ρ_v, may be taken to represent the variation of liquid density with temperature over regions where ρ_v is small in comparison with ρ_l. It has, however, not been generally noticed that if we combine (13) with the equation which represents the law of rectilinear diameters[6],

$$\rho_l + \rho_v = a - bm = 4\rho_c - \rho_c - 2\rho_c m \qquad \ldots\ldots(14)$$

(assuming $\rho_l = \rho_v = \rho_c$ when $m = 1$; $\rho_v = 0$, and $\rho_l = 4\rho_c$ when $m = 0$), we arrive at a reduced equation between density and temperature,

$$\rho = 2\rho_c[(1-m)^{0\cdot3} + 1 - 0\cdot5m], \qquad \ldots\ldots(15)$$

where the subscript l has been dropped[7].

Where the data were available, a logarithmic plot of $\rho/2\rho_c - (1-0\cdot5m)$ against $(1-m)$ was in every instance strictly linear, with a slope corresponding closely to an exponent of 3/10, but in no instance did the line pass through the origin. Most of the cases considered were covered by

$$\rho = 2\rho_c[0\cdot91(1-m)^{0\cdot3} + (1-0\cdot5m)], \qquad \ldots\ldots(16)$$

an equation which represents, to a high degree of approximation, the variation of *orthobaric* density with temperature from freezing point to critical point. The law of rectilinear diameters is another example of a remarkably simple long-range formula. So far as is known, pentane is the only substance for which the law holds exactly, but the deviations in most other instances are very small indeed, amounting to a slight curvature apparent near the critical point, and usually allowed for by the introduction of a small term cm^2 in equation (14)[8].

It would seem then that two remarkably simple relations demand an explanation in terms of modern theory—the power law connecting surface tension and temperature, and the relation between surface-tension and density which is independent of temperature. Professor R. H. Fowler[9] has attacked this second problem by deriving an expression for the parachor which holds in the region of the critical temperature ; he remarks that its validity over the whole liquid range appears to be "somewhat of a happy accident, due to the cancellation of many subsidiary effects". The solution, over the whole liquid range, of these problems, and the provision of a justification for the law of rectilinear diameters would satisfactorily subsume a great mass of experimental results collected by the labours of investigators during the past half-century.

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THE DISTRIBUTION FUNCTION OF A SIMPLE LIQUID MODEL*

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The probability of finding the centre of a molecule in a volume $d\tau$ at a distance R from an arbitrary molecule is usually written as $\rho g(R)d\tau$, where ρ is the macroscopic density. The neighbour distribution function $g(R)$ can be obtained from x-ray scattering data. This function has been widely used in the theoretical study of liquids, especially after its importance was stressed by Bernal[1].

Recently Wall[2] calculated the theoretical distribution function from a shell of neighbours. Each atom was supposed to move freely in a small sphere around a certain point. He fitted his results to the first peak for liquid sodium, and showed that the rest of the curve was approximated by a set of shells of neighbours in the positions suggested by Bernal.

This Einstein model of atoms vibrating independently around the points of a basic lattice has been widely applied to liquids by Lennard-Jones and Devonshire. In a paper which it is hoped will appear shortly, Professor Lennard-Jones and I show that there is a short formula for the distribution function, whatever the shape of the potential well in which each atom moves. This result has been published since by Coulson and Rushbrooke[3]. It takes the form of a rather complicated integral, which does show, however, that $Rg(R)$ from a single shell of neighbours should be symmetrical about a certain value of R. Coulson and Rushbrooke have therefore divided the $Rg(R)$ curve of liquid sodium into symmetrical peaks of arbitrary height and position.

The general result can be expressed as a simple function in at least two cases. Firstly, it reduces to Wall's form when we substitute a potential well. Secondly, the more important case of the parabolic potential can be integrated, and leads to $g(R)=\frac{A}{R}e^{-\alpha(R-R_0)^2}$, where A, R_0 and α depend on the constants of the potential. This is effectively a Gaussian distribution, such as was assumed by Bernal[1] and Prins and Petersen[4] (see figure 1).

We have also carried out a numerical integration for dense gases near the critical point, assuming an intermolecular potential of the form $AR^{-12}-BR^{-6}$. Here the distribution is very flat, and quite unlike the curves calculated by

* A contribution to the discussion on the Liquid State.

de Boer and Michels[5] from the Born-Mayer theory. This can be attributed to the failure of our assumption that the molecules vibrate independently (figure 2).

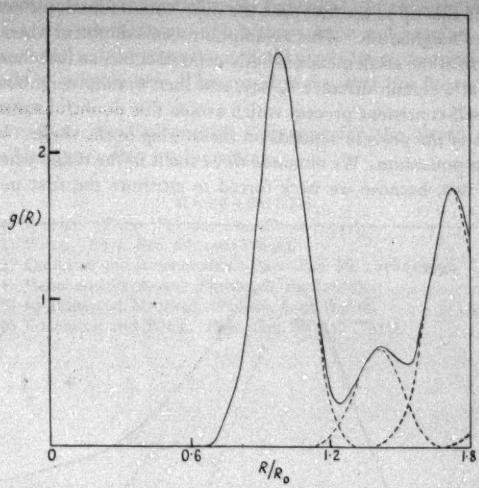

Figure 1. The distribution function produced by motion around the points of a face-centred cubic lattice; the motion is roughly that for argon near its boiling point. Dotted curves are the contributions of successive shells of neighbours. The unit of distance is R_0, the shortest distance between lattice sites.

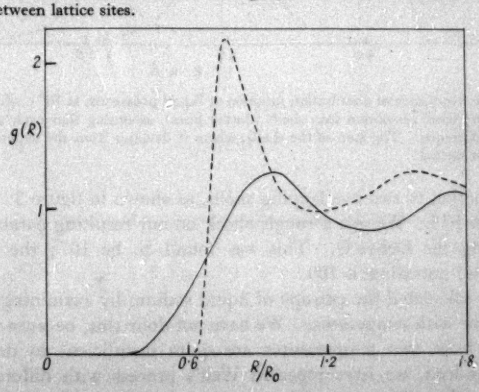

Figure 2. Theoretical distribution functions near the critical point. The full line is the author's result for a face-centred cubic lattice; the dotted line was obtained by de Boer and Michels, from the Mayer-Born theory. The same intermolecular potential was used in these two calculations.

We have cut up the observed distribution function of liquid potassium into a set of Gaussian peaks of arbitrary height, position and half-breadth. Previous workers (Wall[2] (Na), Gingrich and Wall[6] (K), and Coulson and Rushbrooke[3] (Na)) have assumed that up to the first peak the distribution function comes from only a single shell of neighbours. This assumption seems doubtful when we reflect that the solid form of the alkali metals is body-centred cubic, so that there are 8 nearest neighbours at a certain distance r_0, say, and then 6 more neighbours at $1{\cdot}155\, r_0$. We used a self-consistent process which avoids this doubtful assumption. The convergence of the process depends on the overlap of the shells. It proved to be very slow for potassium. We obtained three shells in the range where others have found only two, because we were forced to attribute the first peak in the dis-

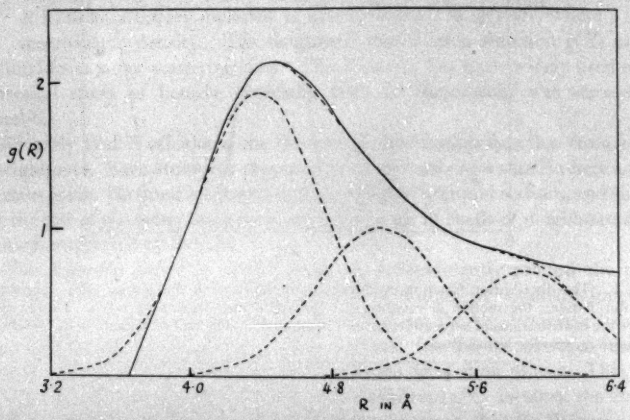

Figure 3. The experimental distribution function of liquid potassium at 70° c. (full line), together with an empirical resolution into shells (dotted lines), assuming that each atom moves in a parabolic potential. The sum of the shells, where it deviates from the experimental curve, is also shown dotted.

tribution function to two overlapping shells, as shown in figure 3. The ratio of their radii is 1·15. We got a rough check on our resulting parabolic potential by calculating the Debye Θ. This was found to be 107; the experimental result for solid potassium is 100.

Wall has calculated the entropy of liquid sodium by examining the variation of free volume with temperature. We have not done this, because we think that calculations from two temperatures are quite insufficient to determine this variation. Indeed, we have repeated Wall's process with different constants but just as good an agreement with experiment, and altered his entropy of fusion by 50 per cent.

The general formula for the distribution function can be inverted by using

Fourier transforms. This means that interatomic forces can be determined from the distribution function of a liquid, via the distribution function of a single shell of neighbours. Unfortunately, the method is very sensitive to errors in the distribution function; also it seems to be impossible to separate the observed total distribution into contributions of arbitrary shape and position, in a unique manner. It is essential to have some theoretical knowledge of the relations between successive shells of neighbours. This problem was first put forward by Bernal and is still unsolved.

I am indebted to the Goldsmiths' Company for the award of a Senior Studentship which made this work possible.

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ON THE THEORY OF HOLES IN LIQUIDS*

By R. FÜRTH, Edinburgh

Read 29 *April* 1940

In a paper published about a year ago in collaboration with Prof. Ornstein and Dr. Milatz in Utrecht, we laid down the general ideas of our theory of holes in liquids. We assume that the structure of a liquid is very similar to that of a solid but that there is an essential difference between them. While the irregularities of the lattice structure of a solid due to the heat movement of the atoms are comparatively small, the liquid is supposed to contain a large number of small holes of the order of magnitude of atomic radii. This structure can be imagined best as the counterpart of the structure of a dense gas or vapour. In such a gas the atoms form small groups or clusters which are formed and destroyed again by the heat movement. If the temperature is lowered or the pressure increased, the frequency of the large clusters increases more and more, and finally, when a certain point is reached, the whole system coagulates into one very big cluster, or the vapour is condensed. This is the fundamental assumption in the theories of condensation of Mayer and collaborators in America and of Born and Fuchs in Edinburgh. In our theory of liquids the holes are the counterpart of the clusters ; they too are formed by the action of the heat movement, and the frequency of the large holes increases more and more, as the temperature is increased or the pressure is diminished. At last, when a certain point is reached, the structure of the system is completely destroyed by the holes, so that it falls to pieces, and this is nothing else than evaporation.

The extremely high fluidity of a gas or a vapour is due to the fact that it consists of parts which have very loose connexions between themselves. On the other hand, the extremely low fluidity of a solid is a consequence of the fact that a flow in a system of atoms forming a lattice can occur only if there are irregularities in the lattice, the theory of which is given in the papers of Lennard-Jones and collaborators on this subject. The great fluidity of a liquid (its essential feature of course) can only be understood if its structure is of the kind mentioned above. Just as in a gas the atoms or clusters of atoms transport momentum by their heat movement, and this phenomenon is responsible for the viscosity, so in a liquid the holes perform a kind of Brownian motion, and the viscosity of a liquid can therefore be explained by the theory of holes in quite a similar manner, taking into account the transport of momentum by this movement of the holes.

In the preliminary paper mentioned above, a rough estimate was made of the number and the size of the holes in the following way : we suppose that the

* A contribution to the discussion on the Liquid State.

difference in volume between liquid and solid is just equal to the total volume of the holes, and that the transition energy (the heat of fusion) is identical with the energy required for the formation of all the holes. We assume further that the energy for the formation of a hole of radius r is approximately equal to $4\pi r^2\sigma$, where σ is the surface tension of the substance. Supposing the holes to be all of the same size to a first approximation, the numbers and the radii of the holes can easily be calculated from the values of the heat of fusion, the surface tension and the increase of volume on fusion. The results are very reasonable: the number of holes is between a tenth and a hundredth of the number of atoms, and the radii of the holes are between one and two atomic radii.

I have improved the theory in the last few months at Edinburgh, calculating firstly the partition function for the radii of the holes on the basis of general statistical mechanics. By this means the average volume of a hole can be expressed in terms of temperature and pressure, and it can be shown that this volume becomes infinitely large when the pressure becomes equal to the vapour pressure of the liquid. It can be shown, however, that there is a region outside this region of normal statistical equilibrium, where the liquid can still exist in a kind of metastable equilibrium. The extent of this region can also be determined and so a statistical treatment of the superheated liquid state can be given. It is further possible, again by means of general statistical methods, to calculate the total number of holes as a function of temperature and pressure, so that the total energy and the total volume of the holes in a certain volume of the liquid can be determined as functions of temperature and pressure. These quantities are closely related to the equation of state and the specific heat of the liquid state. The theory is not yet completed, but I hope to be able to publish the results in a short time.

In addition, I would like to mention that we in Prof. Born's Department of Edinburgh University are now engaged on the improvement of his recent theory of melting and thermodynamics of crystals. Further, I have been able to show that this theory is in good agreement with many facts about melting and the equation of state of solids. Other considerations show that there are close connexions between the phenomena of melting and breaking, as is to be expected according to the fundamental ideas of this theory, and I succeeded very recently in deriving a relation between the tensile strength, the heat of melting per unit of volume and Poisson's elastic constant for isotropic bodies, by a pure thermodynamical consideration, based upon these general ideas; the relation is in perfect agreement with the experiments. A short note on this subject will be found in *Nature, Lond.*, **145**, 741 (1940).

THE SPECIFIC HEAT OF LIQUID METHYL CHLORIDE

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ABSTRACT. The specific heat of liquid methyl chloride has been determined over the range −30° to +30° C. The liquid was in a sealed container provided with a heating coil in a re-entrant tube. Stirring was effected by means of an external solenoid operating on an iron armature. The calorimeter was surrounded by an adiabatic enclosure. The quantity determined experimentally included the latent heat of the liquid vaporized and the heat supplied to warm the vapour in the calorimeter. This was reduced to give the specific heat of the liquid following saturation.

Comparison of data with those of previous investigators indicates good agreement with those of Eucken and Hauck at −30° C. and the extension of the line representing their results over the range from −80° to −30° C. The results given by Shorthose are slightly higher.

§1. INTRODUCTION

Methyl chloride is much used as the working fluid in medium-sized refrigerating plants. Its advantages are that the working pressures under normal conditions are moderate and if a leak develops in the circuit there is little danger from any gas which may escape to the atmosphere[1].

In 1924 the thermal properties of methyl chloride were studied under the auspices of the Food Investigation Board by D. N. Shorthose[2] at the Engineering Laboratory, Oxford. For the determination of the specific heat of the liquid, Shorthose made comparisons of the cooling curves of samples of methyl chloride, alcohol and carbon bisulphide, the fluids being sealed in bulbs with narrow stems. The specific heats assumed for alcohol and carbon bisulphide were stated to be the values given in Landolt and Bornstein's Tables. Shorthose's measurements were made over the temperature range −30° to +30° C. Eucken and Hauck[3] have made measurements of the specific heat between −83° and −33° C. A comparison of the two sets of data shows that the {specific heat, temperature} curves have slightly different slopes near the point of intersection (−30° C.). The present investigation was undertaken as a check on Shorthose's work with a totally different technique. In this case the specific heat was deduced from the temperature rise produced by the generation of a known amount of heat electrically, in a calorimeter from which heat loss was eliminated.

§ 2. DESCRIPTION OF APPARATUS

The sample of methyl chloride was contained in a hermetically sealed copper container A, figure 1, which had been hydraulically tested to a pressure of 10 atmospheres. This container had a stem B and two re-entrant tubes C and D. A heating coil was inserted into C and a ten-way multiple-junction thermoelement into D. The stirrer consisted of two perforated plates carried on a vertical shaft. Attached to the upper end of this shaft was a cylinder of soft iron E located in the stem of the calorimeter. The soft iron was lifted at intervals by sending pulses of current through the solenoid F and returned by its own

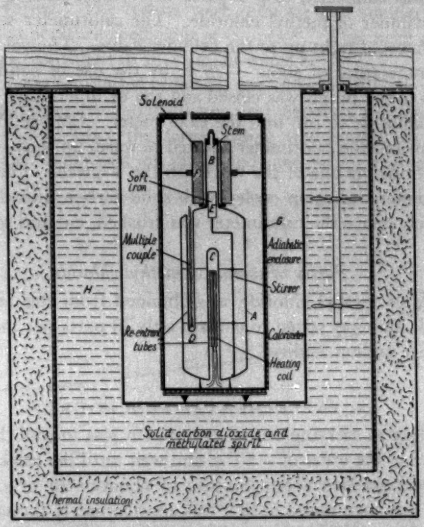

Figure 1. Calorimeter for determining specific heat of methyl chloride.

weight. This solenoid was thermally isolated from the calorimeter by a felt washer at the base and balsa wood wedges at the top. A copper cylinder G surrounded the calorimeter and was provided with a heating coil on its curved side and ends so that its temperature could be varied as required. It stood on three pointed ivory pegs. In an experiment the temperature of this enclosure was maintained the same as that of the calorimeter by controlling the current through the heating coil with a tapping key in the circuit. Outside this adiabatic enclosure was a double-walled vessel H which could be cooled to the desired temperature by a mixture of solid carbon dioxide and methylated spirit. Copper-constantan thermoelements were connected differentially to the calorimeter and adiabatic enclosure G and others between the calorimeter stem and the inside face of the

solenoid. These differential thermoelements were in the circuits of two separate galvanometers. The calorimeter stood on a light ivory ring in the adiabatic enclosure and was held symmetrically by a spider made of a thin cork ring and three pointed ivory rods. The surfaces of the calorimeter and adiabatic enclosure were chromium plated.

§ 3. METHOD OF FILLING THE CONTAINER

A fine-bore copper tube was screwed and soldered into the stem of the calorimeter. This was connected to a T-piece with valves leading off to an exhaust pump and a cylinder of methyl chloride. The calorimeter and pipe-line were heated and exhausted right up to the cylinder valve. The calorimeter was then cooled to a temperature of about $-78°$ c. by the use of solid carbon dioxide; the connection to the pump was closed and the cylinder valve opened, allowing liquid methyl chloride to run into the calorimeter. Connection to the cylinder was next broken and the calorimeter allowed to warm up so as to liberate some of the methyl chloride via one of the valves on the T-piece. This was then closed and the calorimeter was again cooled with solid carbon dioxide and the copper tube immediately above the calorimeter was crushed, cut and soldered.

Purity of sample of methyl chloride

The sample of methyl chloride was obtained from the Imperial Chemical Industries, Ltd., and was stated to contain only 20 parts per million of moisture and 1·5 parts per million acidity.

§ 4. EXPERIMENTAL PROCEDURE

The procedure in carrying out an experiment was to cool the vessel H down to a temperature of the order of $-50°$ c. and wait until the calorimeter and jacket temperatures had reached a temperature of about $-30°$ c. The temperature of the vessel H was then raised until it was approximately the same as that of the calorimeter. Observations were taken of the temperature of the calorimeter so as to determine the rate of drift. Usually this was of the order of $0{\cdot}001°$ c. per minute. The current was switched on to the heating coil and observations taken of the heater current and potential difference at half-minute intervals for a period of five minutes. During the experiment, the stirrer was in operation, the frequency of the impulses to the solenoid being adjusted to maintain temperature equilibrium between the solenoid and the calorimeter. The adiabatic jacket was also maintained in temperature equilibrium with the calorimeter.

After switching off the supply to the heating coil, observations of the temperature of the calorimeter by means of the multiple thermoelement were taken at three-minute intervals until a steady rate of rise was attained. This gradual rise when the calorimeter was below room temperature was due to residual uncompensated heat-leakage along the electrical leads, etc. From these observations

the temperature rise of the calorimeter could be deduced. The conditions were then appropriate for a further experiment, the final rate of drift in the one experiment serving as the initial rate in the following one. Thus the range of temperature from $-30°$ to $+30°$ C. was covered in a series of steps.

§ 5. RESULTS

In order to measure the heat capacity of the calorimeter, the methyl chloride was replaced by distilled water and a series of observations taken. The rate of energy input during these experiments was varied twofold and the duration of heating was also varied. The results were reduced to a standard temperature from the known temperature coefficient of copper[4]. The mean result was that the calorimeter was equivalent to 38·8 gm. of water.*

In the experiments on methyl chloride, two different fillings were used, the depth of liquid differing by about 10 per cent between the two. No greater variation was possible, since the larger filling was limited by the necessity of allowing for the expansion of the liquid, and when the smaller amount

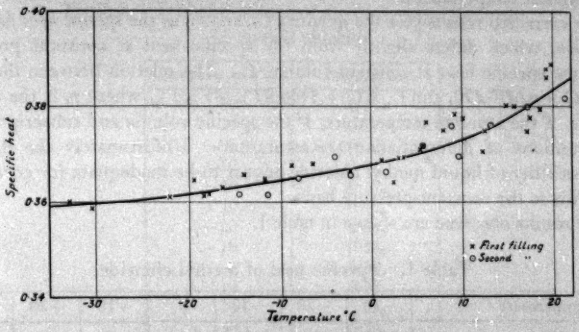

Figure 2. Specific heat of methyl chloride.

of liquid was used, it was necessary to ensure that it was deep enough not to expose the heater tube. In each series, conditions as regards rate of energy input and duration of heating were varied, and from figure 2 it will be seen that the two series are in agreement, and that the uncertainty in the location of the mean line is less than 1 per cent.

The quantity determined experimentally was the total water equivalent of the calorimeter and its contents. From this, the water equivalent of the calorimeter at the mean temperature of the experiment was deducted, and the two-phase specific heat calculated by dividing the remaining water equivalent by the mass of methyl chloride, which in the one series was 333 gm. and in the other 309 gm.

* The calorie used in these measurements is 4·186 joules.

This two-phase specific heat represents the heat required to raise 1 gm. of the contents of the calorimeter through 1° c., and of this heat, part is used in heating liquid, part in heating vapour and part in vaporization. Corrections were applied for the latter two effects, so as to obtain the specific heat of the liquid itself. These corrections were evaluated as follows:—The volumes of liquid at the beginning and end of an experiment were calculated, using the orthobaric densities given by Shorthose, and hence (from the known volume of the calorimeter) the volume of vapour was calculated. The mass of this volume was calculated from the densities given by Shorthose. The heat needed to heat the mean mass of vapour was calculated, assuming its specific heat[5]. The increase in mass of vapour during the experiment was also calculated, and the heat required for its vaporization, using the latent heats given by the present writers[6], furnished the second correction. The weight of liquid was taken to be the total mass of methyl chloride present, diminished by the mean mass of vapour present. It may be noted that in the set of experiments with the larger filling, these corrections never reached 0·5 per cent. In the other set, they were somewhat larger, reaching 1·4 per cent at the highest temperatures.

The corrected results give the quantity C_s, known as the *specific heat following saturation*, which differs slightly from the specific heat at constant pressure, C_p, or the specific heat at constant volume, C_v. The relation between the three is $C_s = C_v + p_s(dV/dT)_s$ and $C_p = C_v + T(\partial p/\partial T)_v\,(\partial V/\partial T)_p$, where p_s is the vapour pressure, T the absolute temperature, V the specific volume and subscripts show the conditions of differentiation (s = saturation). Unfortunately the data on compressibility of liquid methyl chloride appear to be inadequate for correcting our results to the constant-pressure basis.

The results observed are shown in table 1.

Table 1. Specific heat of methyl chloride

Temperature (° c.)	−30	−20	−10	0	+10	+20	+30
Specific heat (C_s)	$0{\cdot}36_0$	$0{\cdot}36_2$	$0{\cdot}36_5$	$0{\cdot}36_9$	$0{\cdot}37_4$	$0{\cdot}38_2$	$0{\cdot}39_0$

§ 6. COMPARISON WITH PREVIOUS OBSERVERS

Only two previous sets of measurements of the specific heat of methyl chloride have been published. Shorthose, by a cooling method, measured the specific heat over the range −30° to +30°c. His samples were enclosed in sealed tubes, and no correction was applied for the latent heat of vaporization or for the heat utilized in raising the temperature of the vapour. His result should thus be slightly high, the error decreasing at the lower temperatures. Eucken and Hauck made measurements at low temperature (−80° to −30° c.) by electrical heating in a vacuum calorimeter. Their results are given as C_s, which at these temperatures is effectively identical with C_p.

A comparison of the three sets of results is given in figure 3. The results of each observer are given at intervals of 10° c., taken from his smoothed curve,

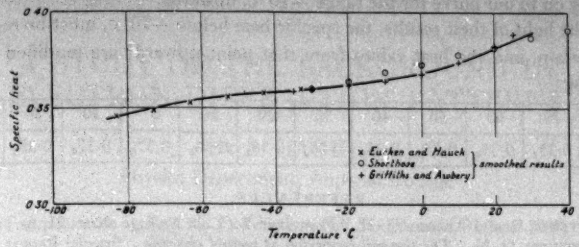

Figure 3. Specific heat of methyl chloride.

and the mean line represents the most probable results, taking into account the whole of the data. These most probable results are given in table 2.

Table 2. Probable values of saturation specific heat of methyl chloride

Temperature (° c.)	Specific heat
−80	$0{\cdot}34_7$
−70	$0{\cdot}35_1$
−60	$0{\cdot}35_5$
−50	$0{\cdot}3i_7$
−40	$0{\cdot}35_9$
−30	$0{\cdot}36_0$
−20	$0{\cdot}36_2$
−10	$0{\cdot}36_5$
0	$0{\cdot}36_9$
10	$0{\cdot}37_4$
20	$0{\cdot}38_2$
30	$0{\cdot}39_0$

§7. ACKNOWLEDGEMENTS

This investigation was carried out as part of the programme of the Food Investigation Board of the Department of Scientific and Industrial Research, and this paper is published by permission of the Director of Food Investigation. Mr. A. Challoner constructed much of the apparatus and also assisted with the observational work.

Note added after completion of this paper

Since writing the above account of our measurements of the comparison with previous observers, we have seen a paper by Messerly and Aston[7] giving the specific heat of methyl chloride from −91° to −23° c. as measured by means of a vacuum calorimeter. Their results pass through a minimum at about

−68° c. and at this point agree closely with those of Eucken and Hauck. From −50° to −20° c. their curve lies below ours, but extrapolated it joins almost perfectly on to our curve for the range −10° c. upwards.

In the light of their results, the specific heat below −70° c. must be regarded as uncertain, and the best values from that point upwards are modified to the following:—

−80	−70	−60	−50	−40	−30	−20	−10	0	10	20	30° c.
($0{\cdot}35_0$)	$0{\cdot}35_2$	$0{\cdot}35_4$	$0{\cdot}35_5$	$0{\cdot}35_8$	$0{\cdot}36_0$	$0{\cdot}36_3$	$0{\cdot}36_6$	$0{\cdot}37_0$	$0{\cdot}37_6$	$0{\cdot}38_2$	$0{\cdot}38_8$

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A STUDY OF THE BACKGROUND IN ELECTRON-DIFFRACTION PATTERNS

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Communicated by Prof. G. P. Thomson, F.R.S. Received 21 *June* 1940

ABSTRACT. Intensity measurements have been carried out on the scattering of electrons by gold films of various thicknesses. The films were prepared by sputtering on cellulosic substrates as well as on rock salt. There was no regularity of scattering for gold films prepared on cellulosic substrates. Gold films prepared on rock salt do, however, give consistent results. The irregularity of scattering of the films prepared on cellulosic substrates was due to a layer of the cellulosic substrate, which was interlocked in the gold films in such a way that it could not be removed by repeated washing. Detailed absolute measurements were made of the background for two gold films, 395 A. and 750 A. in thickness, prepared on rock salt. The distribution function of the background is practically constant within the range from 2° to 4°. A uniform background like this is probably due to plural inelastic scattering accompanied by diffuse scattering due to the thermal motion of the atoms in the crystallites.

§ 1. INTRODUCTION

A NUMBER of experiments[1] have been carried out for the determination of the intensities of the rings in the electron-diffraction patterns of microcrystalline foils in order to solve problems concerning crystal structure and to give quantitative data for the test of the theory of the intensity of rings. Very little attention has been directed to finding out the nature of the continuous background on which the rings are superimposed. The normal experience of workers[2],[3] in the field of fast electrons tends to show that the background increases on lowering the energy of the electrons or on taking a thicker foil. The sharpness of the rings does not greatly change, but they gradually lose contrast with the background. No quantitative measurement has yet been carried out on the variation of the background scattering with different energies of the electrons or with different thicknesses of the scattering foil at a constant voltage. Some investigators[4],[5],[6] have studied the angular distribution of the background scattering, but their experimental results are very meagre. The determination of the angular variation of the background scattering is of interest, as this will form an experimental basis for a theory of background scattering.

The purpose of the present investigation is to determine how the intensity of the general background (within a fixed angular range of scattering) varies

relative to the transmitted beam with different thickness of the scattering foil and also for different energies of the electrons. A knowledge of this factor will enable us to find out the most favourable conditions for observing the diffraction patterns. It is also desired to find out, for a few films, the fraction of the incident electrons that goes to form the central spot and also the fraction that is scattered in the background per unit solid angle. From the latter measurement we can draw what we may call "the electron distribution curve" of the background.

An electrical method has been utilized for measuring the intensity of the electrons. Thin films of gold were used as the scattering material.

§ 2. DESCRIPTION OF THE APPARATUS

The electron-diffraction camera used was a modification of that designed by Professor G. P. Thomson[7] (figure 1). A very short description of the parts that were modified for the purpose of the intensity measurement is given below.

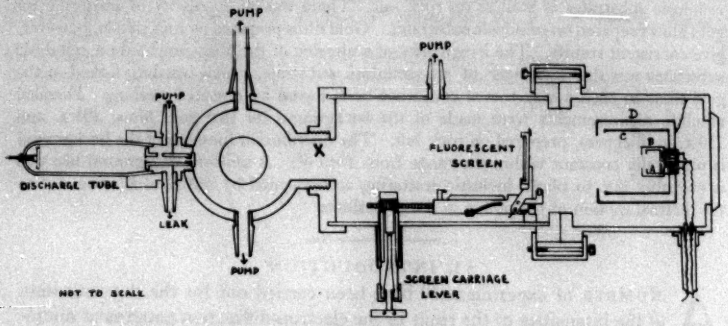

Figure 1.

(*a*) The Faraday cylinder for the study of the general character of the background can be seen in figure 1. It consists of four co-axial brass cylinders, insulated from each other by amber bushes. The inner cylinder A had a front opening, 6·5 mm. in diameter. It was surrounded by the cylinder B, with an opening of 4·98 mm. diameter. The large cylinder C had an opening of 6·33 cm. diameter and was surrounded by the cylinder D, which was permanently earthed; its front opening was 6·01 cm. in diameter. The cylinders were supported by a small brass stand inside a chamber which was clamped to the main body of the camera. The leads from the cylinders B and C were jointly connected to a terminal passing through an amber bush in the wall of the outer casing in which the cylinders were accommodated. The lead from A was connected to a separate terminal in the same insulated bush. Connections between these two terminals and the detecting system were made by thick copper wires supported in an earthed brass tube by amber bushes.

(*b*) The arrangement of the cylinders for the measurement of the angular scattering is shown in figure 2(*a*). The inner cylinder *a* has a front opening *f*, 4 mm. in diameter. It was surrounded by the annular cylinder *b*, and the width of its front opening *g* was also 4 mm. The outside cylinder *c* was the earthed casing which carried the front cover *d*, shown separately in figure 2(*b*). The cover *d* was divided into two parts by an annular slit *e*, 1 mm. in width. The two parts were joined together by three brass strips *i*, each 0·5 mm. in width. The circular opening *h* in the middle of the cover *d* was immediately in front of the opening *f*, and the annular slit *e* was just in front of the opening *g*. The mounting

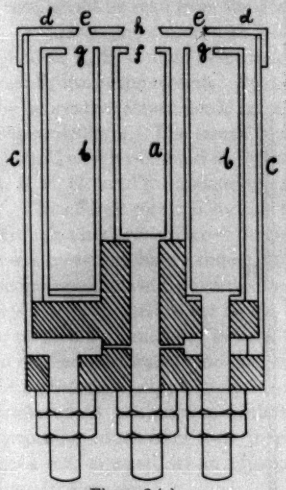

Figure 2 (*a*).

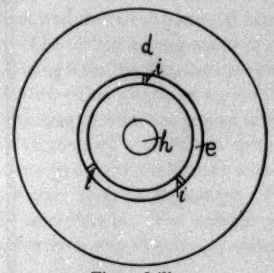

Figure 2 (*b*).

of the cylinders is shown in figure 3. The outside earthed casing *c* was connected to a frame *j* which was carried by a tubular nut *k*. The tubular nut was again keyed in the housing *l*, which was fixed to the long brass casing *m*. It was also engaged with the central screw *n*, which was housed at its back end inside the bracket *o*. In order to get rid of back-lash of the screw *n*, two collars *p* were pinned on each side of the bracket *o*. The screw could be rotated by a handle attached to a solid brass cone, ground to fit into the end of the supporting brass casing *m*. The coupling of the cone to the screw was effected by two pins *q* fastened at the end of the cone. The screw *n* had a working length of 40 cm. and was of 2 mm. pitch. The leads from the cylinders *a* and *b* were connected by two springs to two terminals in the wall of the brass casing *m*. The terminal that connected the spring from the annular cylinder was made longer so that the two springs might not touch each other or any other part inside the camera. The other end of the

longer lead was supported at the wall of the casing *m* by amber. The connection between these two terminals and the detecting system was made, as before, by

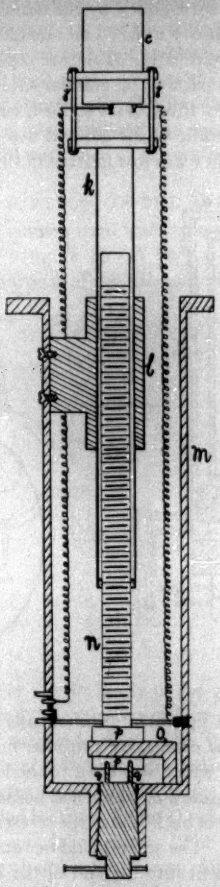

Figure 3.

means of two thick copper wires supported in an earthed brass tube by amber bushes.

For the purpose of the measurement of the angular scattering of the electrons, the fixed cylinders used in the preliminary experiment described above in (*a*)

were removed and the brass casting *m*, which carried the Faraday cylinders *a*, *b*, *c* and *d*, was fitted at the back of the camera. By turning the handle attached to the cone at the back of the casing *m*, the Faraday cylinders could be moved backward and forward inside the camera. A "Veeder" counter (not shown in figure 3) was fixed on the brass casing *m* just above the cone to count the number of revolutions of the screw *n*, which determined the distance traversed by the Faraday cylinders. The cone was graduated into 20 equal divisions in front of the handle and a zero mark was placed on the main housing of the cone. Each complete rotation of the cone was recorded by the "Veeder" counter and shifts less than 2 mm. could be read from the graduation mark on the cone.

A fluorescent screen was fitted inside the camera just in front of the fixed cylinders A, B, C and D (see figure 1). The screen was usually held down horizontally inside the camera. By turning a greased cone from outside the apparatus, the fluorescent screen could be raised up so that the electron beam could strike it perpendicularly. The screen could be viewed through a window (not shown in figure 1) which was fixed on the body of the brass casing that carried the cylinders A, B, C, D, used for measurement of the general background.

The charge received by the Faraday cylinders was allowed to leak to earth through a high resistance of the order of 10^{12} ohms, and the fall of potential across it was measured by a Lindemann electrometer. The circuit arrangement of the electrometer was of the usual form. The leads coming from the Faraday cylinders could be connected to the needle of the electrometer, either jointly or separately, or earthed by a mercury switch. The whole detecting system was placed inside an earthed perforated zinc box, which provided satisfactory shielding in spite of the high-tension supply in the room. The high-tension circuit was the one usually employed in conjunction with the Thomson-Fraser type of apparatus. The smoothing condensers were increased to 0·012 microfarads. The voltage was measured, as usual, by an adjustable spark gap between two aluminium spheres 5 cm. in diameter.

§ 3. PREPARATION OF METALLIC FILMS

The gold films which were used for the intensity measurements were prepared by cathode sputtering. As a substrate for sputtering, a thin skin of collodion, celluloid, or cellulose acetate was used. Besides these, some films were also prepared by sputtering on polished rock salt. The technique for preparing the cellulosic substrates was the same as that developed by F. Jolliot and by Professor G. P. Thomson[2]. The sputtering was carried out under various conditions of current and Crookes dark space. The distance of the substrates from the cathode was also altered. The films were manoeuvred over aluminium discs pierced with holes of 1·7 mm. diameter. The thickness of the gold films was determined by measuring the percentage of white light transmitted by the films with the help of a Cambridge Recording Microphotometer, using the experimental data given by Schulze[8] for wave-length 4920 A.

§4. EXPERIMENTAL PROCEDURE FOR THE MEASUREMENT OF THE GENERAL BACKGROUND

A magnet was fixed near the anode. The inner cylinder A (figure 1) was connected to the electrometer and B and C to earth. By altering the position of the magnet, the beam was allowed to enter the inner cylinder A. The magnet was moved in all possible directions till the maximum deflection was recorded in the electrometer, and the magnet was then clamped in this position.

In the present investigation it was not desired to get an absolute measurement of the scattering, but the total number of electrons that entered the large cylinder C outside the opening of B was compared with the transmitted electrons that entered A. The transmitted electrons were limited by the opening of B, which allowed the total number of electrons in a cone of semi-vertical angle 16 minutes to enter into A. Only electrons which were scattered within 3° 33′ could enter the large cylinder C. In order to find out the ratio of the scattering, the discharge was maintained at a constant voltage. Then the cylinders A, B and C were connected to the electrometer and the deflection observed. The potential drop across the high resistance corresponding to the above deflections was read from the calibration curve of the electrometer. If I_1 was the potential drop due to the leakage of electrons that entered into the cylinders A, B, C, and I_0 that due to electrons that entered A, then our measurement gave the value of $(I_1-I_0)/I_0$.

No difficulty was found in keeping the beam at a constant voltage for about five minutes if the current through the discharge tube was very small. The tube current was not more than 10 μa. in the above experiment. The electrometer needle took several minutes to attain its steady position, so observations were taken for times in the ratio of the capacities of the cylinders A, B and C together, to the capacity of A alone. This ratio was determined by a preliminary experiment to be 1·71. Deflection was observed for 51 seconds for A, B and C joined together, and for 30 seconds for A alone. The time of deflection was determined by using the intermittent noise of a buzzer operated by a pendulum beating seconds, which closed the circuit once in each vibration.

§5. RESULTS OF THE MEASUREMENT OF TOTAL SCATTERING

The ratio of the scattering from 16′ to 3° 33′ to the transmitted beam (denoted by $(I_1-I_0)/I_0$) was determined at different voltages. Figure 4 shows two typical curves of this sort. Curve 1 is for a film, 120 A. thick, which was prepared on celluloid. The film is denoted by G_C 1 (G_C means a gold film prepared on a cellulosic substrate). Curve II is drawn for another film, G_C 2, 270 A. thick, which was prepared on collodion. From the set of curves for the various films the ratio at 30 kv. was noted. In figure 5 the ratio at 30 kv. is plotted for all films prepared on cellulosic substrates, and in figure 6 for the films obtained from rock-salt substrates. Some of the films are specified by numbers for reference. From the study of figures 5 and 6, it appears that there is no regularity of the ratio for the films obtained for cellulosic substrates. The results for the films obtained for rock-salt substrates do, however, lie on a single curve.

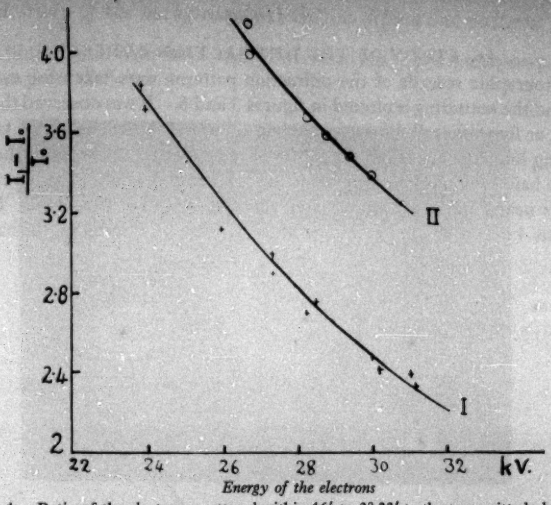

Figure 4. Ratio of the electrons scattered within 16′ to 3° 33′ to the transmitted electrons, shown as a function of the energy of the incident electrons.

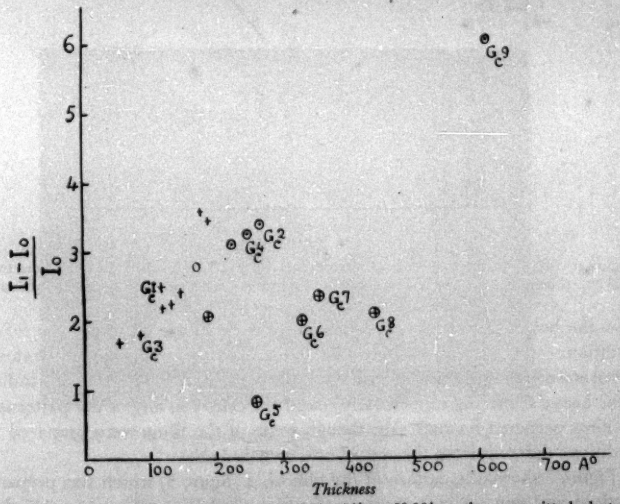

Figure 5. Ratio of the electrons scattered within 16′ to 3° 33′ to the transmitted electrons at 30 kv., shown as a function of thickness, for gold films collected from cellulosic substrates.

⊙ Gold film prepared on collodion.
\+ ,, ,, ,, celluloid.
⊕ ,, ,, ,, cellulose acetate.

§6. STUDY OF THE DIFFRACTION PATTERNS

Photographic records of the diffraction patterns were taken for most of the films, and the scattering is plotted in figures 5 and 6. It was observed that, except for four or five films, all films prepared on cellulosic substrates gave a very heavy scattering immediately round the centre of the patterns. In some of the patterns a diffuse halo could also be seen inside the (111) ring of gold. The spacing of the halo was nearly the same in all plates where it could be measured. The mean value was $4{\cdot}48 \times 10^{-8}$ cm. The few films ($G_C 5$ to $G_C 9$ in figure 5) that did not

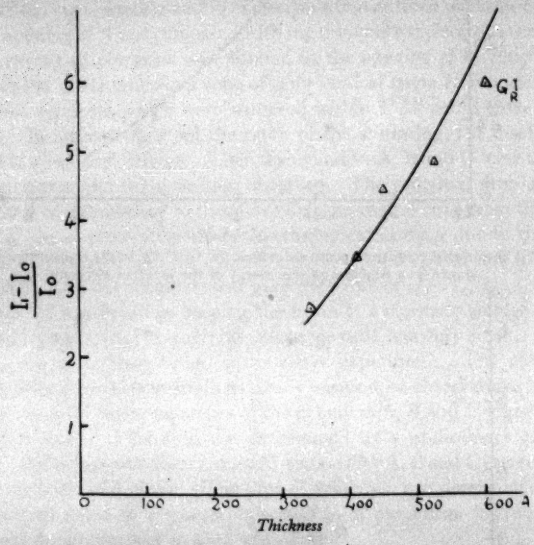

Figure 6. Ratio of the electrons scattered within 16′ to 3° 33′ to the transmitted electrons at 30 kv., shown as a function of thickness, for gold films collected from rock-salt substrates.

show the heavy scattering round the centre were sputtered under the following condition:—the current was less than 2 ma. and the cellulosic substrates were placed at a distance less than 0·5 cm. from the dark space. There was no indication of the heavy scattering immediately round the centre in any of the patterns from the films prepared on rock salt, though some of the films were prepared under conditions different from the special one, as noted above.

Figure 7 shows the pattern of the film $G_C 3$ (figure 5) which was prepared on celluloid, and figure 8 is the pattern of a film, $G_R 1$ (figure 6), where G_R denotes a gold film prepared on rock salt. The film $G_R 1$ was 600 A. in thickness. It is a very interesting fact that, for a film as thick as 600 A. when prepared on rock salt, the rings are not merged into the background. Cochrane[3] did not get any pattern

from gold films thicker than 500 A. with 32 kv. electrons. His films were prepared by sputtering on celluloid.

Figure 7. Electron-diffraction pattern of a gold film (90 A. thick) prepared on celluloid.

Figure 8. Electron-diffraction pattern of a gold film (600 A. thick) prepared on polished rock salt.

The films prepared on a cellulosic base were pink, colourless or bluish green by reflection, while the films prepared on rock-salt substrate were always reddish yellow in colour.

§7. MEASUREMENT OF THE ANGULAR SCATTERING OF THE BACKGROUND

The Faraday cylinders used for the measurement of the angular distribution of the background have already been described. In this section of the work, the steady deflection of the electrometer needle was observed. The current in the discharge tube was increased to 0·5 ma. and the smoothing condenser was increased to 0·03 μF., for in this way it was possible to keep the beam steady for a considerable period of time.

The beam was adjusted as before, so that it could enter the inner cylinder *a* unobstructed. The specimen was brought in the path of the beam. The beam being maintained at 30 kv., the electrons which entered the inner cylinder *a* were

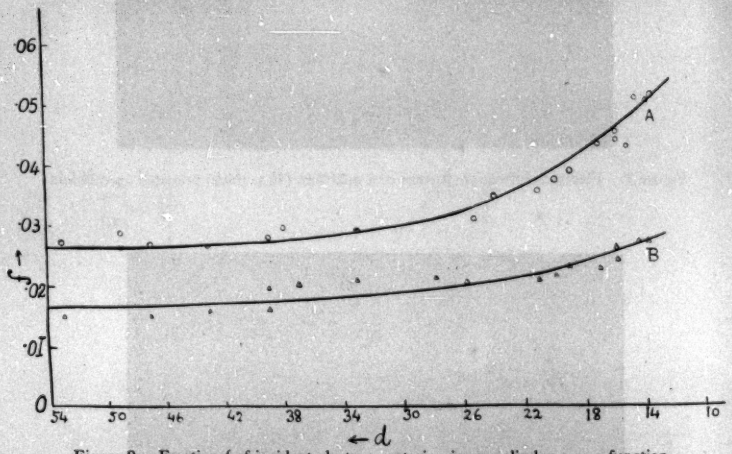

Figure 9. Fraction *f* of incident electrons entering inner cylinder *a* as a function of distance *d* of cylinder from specimen.
Curve A. Gold film G_C 12 (480 A.).
„ B. „ „ G_B 3 (750 A.).

compared with those which entered the cylinders *a* and *b* at several positions of the cylinders inside the camera. A different experiment was carried out to compare the electrons that entered the inner cylinder *a*, with the main incident electrons at several positions of the cylinders inside the camera. For the measurement of this factor the film could be taken in and out of the path of the electrons by a lever operated from outside the specimen chamber. The fraction of the incident electrons that entered into the cylinder *a* at different positions was now plotted against the distance of the cylinder from the specimen. A smooth curve was drawn through the points (cf. figure 9, which shows the curves for two gold films). With the help of the above curve the electrons that entered the annular cylinder

at several positions were now expressed as a fraction of the incident electrons. From the known dimensions of the Faraday cylinders, the solid angle subtended by the annular slit at the specimen was calculated for the various positions where measurements were taken with the cylinders *a* and *b*. The angle of deviation of the scattered electrons was also calculated for all these positions. The fraction of the incident electrons that entered into *b* at various positions was transformed to the fraction of the incident electrons scattered per unit solid angle. This fraction is denoted by $f(\theta)$.

When the Faraday cylinders were at the extreme back position (i.e. when the cylinders were 52·94 cm. away from the specimen), the annular cylinder could catch the electrons which were deviated through an angle of 1°·03. Also the present arrangement did not permit the measurement of electrons deviated through more than 4°·03. It was, however, possible to draw the distribution curve below 38′ from the curves, as shown in figure 9, from the following considerations:—

If I_1/I_0 be the fraction of the incident electrons that enter into the inner cylinder *a* when the half-angle subtended by its opening at the specimen is θ_1, and if I_2/I_0 be the corresponding fraction when the angle is θ_2, then

$$\frac{I_2}{I_0}-\frac{I_1}{I_0}=\int_{\theta_1}^{\theta_2}2\pi f(\theta)\sin\theta\,d\theta.$$

If d_1 and d_2 be the distances of the Faraday cylinder from the specimen when the half-angles subtended by its aperture at the specimen are θ_1 and θ_2, and r_0 be the radius of the central opening *h*, then

$$\frac{I_2-I_1}{I_0}=2\pi f(\bar{\theta})\frac{r_0^2}{2}\left(\frac{1}{d_1^2}-\frac{1}{d_2^2}\right).$$

$\left(\text{Under the assumption that } \theta_1 \text{ and } \theta_2 \text{ are very close together, } \bar{\theta}\sim\frac{\theta_1+\theta_2}{2}.\right)$

The distribution function, as calculated from the above relation, is rendered inaccurate because the curve, as shown in figure 9, from which the distribution function is to be calculated cannot be drawn very accurately owing to the wide spread of the points. Besides this, there is another source of error. When the Faraday cylinder is taken more than 28 cm. forward from its back position, it goes very close to a narrow neck (marked × in figure 1) between the specimen chamber and the main body of the camera. So it is quite certain that the Faraday cylinder will catch some of the scattered electrons when it is taken close to the neck; thus we cannot place too much reliance on the part of the curve below 38′.

§8. RESULTS OF THE ANGULAR-SCATTERING MEASUREMENT

(a) *Results for the gold films*

The gold films used for the study of the angular distribution of the background in this section were not previously used for the study of the total scattering. Figure 10 shows the background distribution curve of three gold films, prepared

on collodion. Curve A is for a film, G_C10, 75 A. thick, and curve B for another film, G_C11, 125 A. thick. Both the films G_C10 and G_C11 were prepared by sputtering with a current higher than 3 ma. Curve C shows the background distribution for another gold film, G_C12, 480 A. thick. This film was prepared with a current less than 2 ma., and the collodion base just touched the Crookes dark space.

In figure 11 we have shown similar curves for two gold films, G_R2 (395 A. thick) and G_R3 (750 A. thick). These two films were prepared by sputtering on

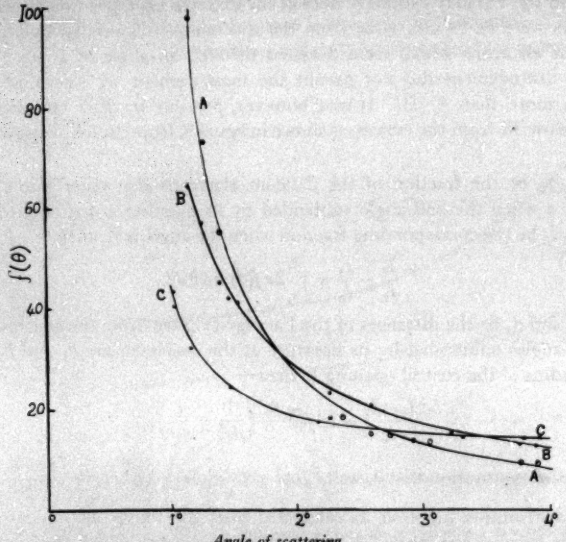

Figure 10.

⊙ Curve A. Film G_C10 (75 A. thick).
● ,, B. ,, G_C11 (125 A. ,,).
⊡ ,, C. ,, C_C12 (480 A. ,,).

rock salt. In the above determination of the angular distribution of the background some measurements were also taken on the rings. But the rings could easily be eliminated by drawing a smooth background curve. In figure 11 the measurements on the rings are also shown. The positions of the rings are indicated along the abscissa. The small portion of the distribution curve below 38′ is not shown in the above curves.

An examination of all the curves in figures 10 and 11 reveals that the intensity distribution curves of the background for the films prepared on collodion are quite different from the curves for the films prepared on rock salt. Further,

the curves for the films prepared on collodion are not all quite similar. The curves become less steep at smaller angle, with increasing thickness. The curves for the films $G_R 2$ and $G_R 3$ (prepared on rock salt) are practically horizontal between 2° and 4°, and also there is very small difference in the absolute values of the distribution function of the background, though the thickness increases by a factor of two.

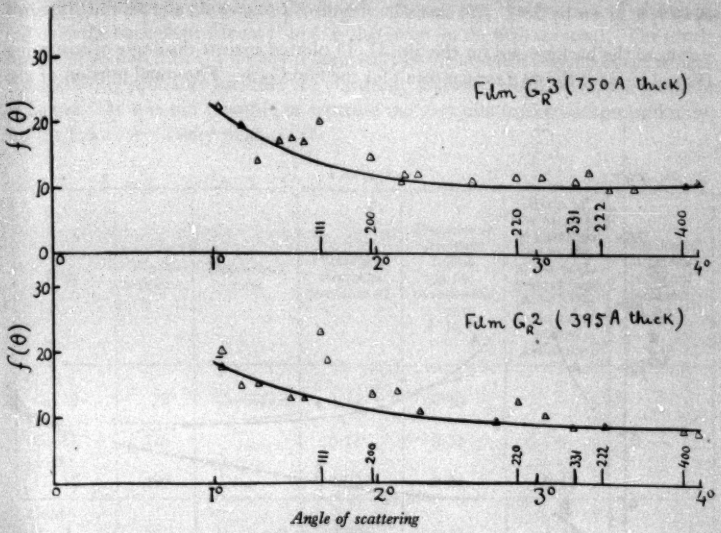

Figure 11.

(b) *Results of the measurements on a collodion film*

The angular distribution of the scattering was also measured for a collodion film, C 1, of thickness ~570 A. The film was so thin that no interference colour could be seen from it. In order to determine the thickness of the thin collodion film, two thicker films were made which showed interference colours. The thicknesses of the films were estimated from the measurement of the interference fringes by reflection. From the determination of the fraction of electrons transmitted through the films, the absorption coefficient μ was calculated. The length μ^{-1} at 30 kv. was about 810 A. for collodion. Knowing the absorption coefficient, the thickness of the thin collodion film was estimated by a similar measurement of the fraction of electrons transmitted through the film. (The fraction of electrons transmitted is defined as the amount caught by the inside Faraday cylinder *a* in its back position to the amount caught by the same cylinder in the same position under the same condition when the film was moved out of the beam.) The

angular distribution of the scattering for the film C 1 fits the background distribution curve for the film $G_C 10$ (figure 13) not only in shape but also in absolute magnitude between 1° and 4°. This point is considered later on in § 10.

§ 9. GENERAL MAGNITUDE OF THE BACKGROUND

The total number of electrons scattered between the limit of angle from θ_1 to θ_2 is given by $2\pi \int_{\theta_1}^{\theta_2} f(\theta) \sin\theta \, d\theta$. Figure 12 (curve A) shows the $f(\theta) \sin\theta$ values of the background for the film $G_C 11$ plotted against the angle of scattering (θ) and curve B shows a similar result for the film $G_R 3$. The small portion of the

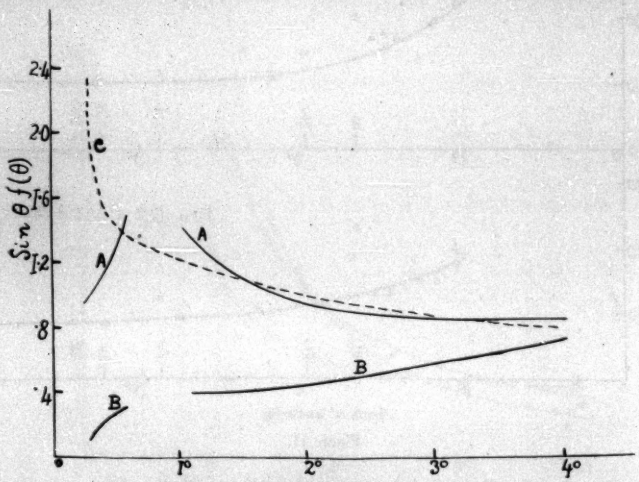

Figure 12.

Curve A. Gold film $G_C 11$.
„ B. „ „ $G_R 3$.
„ C. „ „ (150 A.) (P. White).

curves below 38′ is here shown. Curve C shows the values of $\sin\theta f(\theta)$ in arbitrary units for a gold film ~150 A., as determined by P. White [4]. The curve C is drawn so as to fit curve A at 1°·5. It can be seen that White's curve is almost similar to our curve A beyond 1°·2, but it shows the steep rise at a smaller angle. There is thus a discrepancy between our results and those of White at a smaller angle. The reason for this is not clear.

In order to compare the results of the films used for the angular scattering measurements with the others used for the study of the general background (see § 6) we have to integrate the $\sin\theta f(\theta)$ curves from 16′ to 3° 33′. But there is

a gap in the sin $\theta f(\theta)$ curves from 38′ to 1°. It is possible to interpolate the curves in this intermediate region for the films $G_C 12$, $G_R 2$ and $G_R 3$, but not for $G_C 10$ and $G_C 11$, as the sin $\theta f(\theta)$ curves for $G_C 10$ and $G_C 11$ show a very high peak within this region of angle. The ratio of the electrons scattered in the background from 16′ to 3° 33′ to the transmitted electrons is tabulated in the sixth column of table 1 for the films $G_C 12$, $G_R 2$ and $G_R 3$. The fraction of electrons transmitted through the films is shown in the fourth column, and the fraction of electrons falling in the background from 1° to 4° is also given (in the fifth column). The result for the collodion film C 1 is shown separately in the seventh column because here the scattering probably includes the elastically scattered electrons which give rise to haloes. It was not possible to separate the part due to the background only, for the haloes were very weak.

Table 1

Film	Thickness in A.	Depositing base	Fraction of electrons transmitted	Fraction of electrons falling in the background from 1° to 4°	Ratio of the number of electrons scattered in the background from 16′ to 3° 33′ to the transmitted electrons	Fraction of electrons scattered between 1° and 4°
Gold: $G_C 10$	75	Collodion	0·25	0·30	—	—
Gold: $G_C 11$	125	,,	0·11	0·31	—	—
Gold: $G_C 12$	480	,,	0·027	0·25	9·16	—
Gold: $G_R 2$	395	Rock salt	0·076	0·14	1·84	—
Gold: $G_R 3$	750	,,	0·015	0·17	10·53	—
Collodion: C 1	570	—	0·48	—	—	0·30

The Faraday cylinder *a* could catch the electrons within 9·7 minutes of deviation when it was at the back position. So we can compare the results, tabulated in the sixth column, with the results of section 5, if we neglect the background from 9·7 minutes to 16 minutes. It can be seen that the gold film $G_R 2$ gives a ratio 1·84, which lies far below the curve in figure 6. It should be increased by about 50 per cent to fit the curve in figure 6. This inconsistency in the result is most probably due to the error in drawing the distribution curve below 38 minutes, and also to the neglect of the rings in the measurement of the angular scattering. It is not at all justifiable to neglect the rings when the background is very small. The rings, as observed on the screen, for the film $G_R 2$ were very intense. The film $G_R 3$ gives the high ratio 10·53. No total scattering

measurement was carried out with such a thick film, prepared on rock salt, but if we extend the curve of figure 6 towards higher thickness it can be seen that the above ratio lies above the curve. But it is possible to draw another curve through the points in figure 6, which, if produced beyond 600 A., will pass very close to the above point. So we do not think that the high ratio of scattering for the film $G_R 3$ is due to any difference between the nature of this film and the others prepared on rock salt, which were used for the total scattering measurements.

§ 10. GENERAL DISCUSSION

The discussion of the results of the experiments, as described above, falls into two parts: (*a*) the experiments dealing with the background scattering for pure gold, and (*b*) those which elucidate the discrepancy between the results for gold films prepared on rock salt and on collodion.

(*a*) Detailed absolute measurements were made of the background scattering for two gold films ($G_R 2$ and $G_R 3$ respectively) 395 A. and 750 A. in thickness, which were prepared on rock salt. These measurements should form the basis of a theory of a background scattering, as so far no theory has been given. Several factors are to be taken into account in forming a theory. Firstly, there is the scattering due to heat motion which gives a diffuse background in the case of x rays and which can be expected to give a similar background in the case of electrons. Secondly, the inelastic scattering should also contribute to the background. According to the theory of Morse[9], the inelastic scattering should fall off rather quickly with angle, if it were single scattering. On the other hand, the experimental results indicate that the scattering is practically constant beyond 2°. The thicknesses of the films used were such that plural scattering certainly took place, and it is possible that this may be the reason for the discrepancy between the results and the theory.

(*b*) The results of the study of the general background (§ 5) show that there are large variations of the background scattering for gold films of approximately the same thickness, when prepared on cellulosic substrates. For example, the film $G_C 4$ (figure 5) gave a ratio of the scattering from 16′ to 3° 33′ to the transmitted beam (as defined in § 4), which is four times higher than the corresponding ratio for the film $G_C 5$. Both the films are nearly 250 A. in thickness. Moreover, there is no regularity when the ratio is plotted as a function of thickness (figure 5). Gold films prepared on rock salt do, however, give consistent results (figure 6). The results of § 8, where the distribution function $f(\theta)$ for the background scattering is determined in absolute measure, show that the distribution $f(\theta)$ for the gold films prepared on rock salt is quite different, both in magnitude and shape, from those prepared on cellulosic substrates.

Besides this, the fraction of electrons transmitted through the films shows a completely different dependence on thickness, e.g. a 125-A. gold film ($G_C 11$) from collodion base transmitted 0·11 of the incident electrons, while on the other hand, a 395-A. gold film ($G_R 2$) from a rock-salt base transmitted 0·076 of the

incident electrons (see table 1). On this basis one would have expected a fraction of about 0·45 to be transmitted through a film of gold 125 A. thick. It is clear, therefore, that there is some extra scattering material in the film $G_C 11$, equivalent in scattering power to a film of gold of thickness ~200 A. There are several possibilities which might account for the extra scattering:

(i) absorbed or adsorbed gas;

(ii) "amorphous" gold;

(iii) collodion from the substrate which was not removed by the solvent.

It is impossible to exclude the presence of absorbed gas in a sputtered film, but in order to give the very large extra scattering it would be necessary to postulate a very great quantity of gas (air). Layers of the order of thousands of angstroms in thickness would be necessary. This is hardly conceivable.

As regards the "amorphous" gold, which some investigators think possible, it would be necessary to assume that the "amorphous" gold did not affect the thickness of the film as measured by its absorption of light. This is in itself hardly likely. Experimental evidence has been accumulated in favour of the fact that when films are bombarded by electrons, the crystals on the films grow in size. So we can expect that prolonged bombardment of the electrons would have caused crystallization of the amorphous gold[10] in the films. However, no change of thickness was observed when the 125-A. thick film ($G_C 11$) was measured again after it had been subjected to bombardment lasting several days in all. Moreover, no change was observed in the absolute values of the distribution function $f(\theta)$ when the observation was repeated after two or three days.

The remaining possibility is that some of the base had been interlocked into the structure of the gold film in such a way that it could not be removed by prolonged washing. There is no other possibility, for the interior of the bell jar where sputtering was carried out was kept as clear as possible, so that there is no possibility of any foreign material being deposited on the film during the time of sputtering. It is possible to subject the hypothesis to a severe test. If the films formed on a collodion base do indeed contain a fair quantity of collodion, then a very thin gold film, prepared on collodion, should show a distribution curve $f(\theta)$ which is characteristic not of gold but of collodion. The test was carried out by preparing a gold film, $G_C 10$, 75 A. thick, on a collodion base and a film of collodion, C 1, 570 A. thick. The film was chosen to be roughly of the thickness of collodion suspected to be contained in the gold film. Figure 13 shows the distribution function of the above two films. It can be seen that the curves fit perfectly in shape. Hence one may take it as certain that so-called gold films of 75 A. contained a layer of collodion several hundred angstroms in thickness. The fact that the magnitudes of the two curves practically fit together is of no practical significance because the fraction of electrons transmitted through the films is actually different (see table 1). This is probably due to plural scattering. This effect was also observed in the case of the films $G_R 2$ and $G_R 3$ (see figure 11).

It was shown above that some of the films prepared on cellulosic substrates showed a diffuse halo; the spacing was very nearly equal to a spacing of celluloid[11]. Hence one may take it as established that the discrepancy between the results for gold films prepared on rock salt and on collodion or other cellulosic base is only due to the part of the cellulosic base which was not removed by washing.

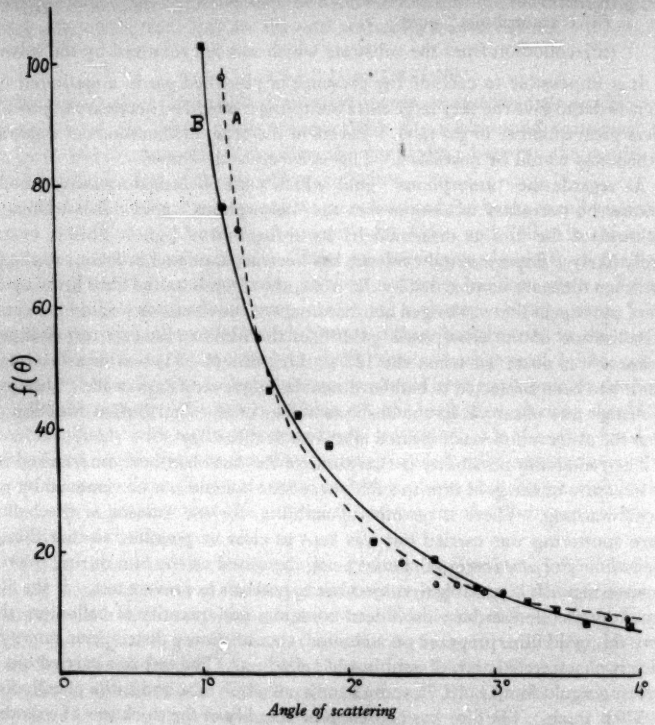

Figure 13.

⊙ Curve A. Gold film G_C 10.
⊞ „ B. Collodion film C 1.

The absorption coefficient of a few pure gold films, prepared on rock salt, was determined from the measurement of the fraction of electrons transmitted through the films. It was about $6{\cdot}25 \times 10^5$ cm^{-1} By the same procedure the absorption coefficient of collodion films was found to be $1{\cdot}23 \times 10^5$ cm^{-1} From these values it was possible to calculate how much collodion was left in the various

gold films used for the scattering measurements. The following table shows the thickness of collodion left in the gold films.

Table 2

	Film G_C 10	Film G_C 11	Film G_C 12
Optical thickness of the gold films	75 A.	125 A.	480 A.
Thickness of the collodion film remaining in the gold film	730 A.	1135 A.	565 A.

It is very interesting to note that the collodion film left in the films G_C 10 and G_C 11 is about ten times as thick as the corresponding gold film.

The film G_C 12 was sputtered with a current less than 2 ma. and the collodion base was placed at a distance less than 0·5 cm. from the dark space (see § 9). When a film is prepared under this condition one cannot expect a heavy scattering immediately round the central beam (§ 7), but the film still contains a fair amount of collodion.

ACKNOWLEDGEMENTS

I should like to express my gratitude to Professor G. P. Thomson for providing the facilities for the work, for suggesting the problem, and for helpful guidance. My thanks are due to Dr. M. Blackman and Dr. W. Cochrane for help and criticism in all stages of the work. I should also like to express my thanks to the Government of Bengal (Educational Department) for a scholarship from the Mohsin Endowment Fund which has enabled me to devote my time to this investigation.

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THE DIELECTRIC PROPERTIES OF SOME THERMOPLASTICS*

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ABSTRACT. The paper describes an investigation of the electrical properties of a series of pure thermoplastics, five of them being phenolics prepared by the condensation of phenol, *o*-, *m*- and *p*-cresol, and *m*-5 xylenol respectively with formaldehyde, and one being derived from benzyl alcohol. It is shown that the dielectric behaviour of all these materials is essentially similar, and that it is characterized by a sharp peak in the curves representing power factor as a function of either temperature or frequency, accompanied by a relatively rapid change of dielectric constant. The changes both of power factor and of dielectric constant are approximately proportional to the concentration of hydroxyl groups in the resin, showing that these properties depend on molecular structure. They are interpreted as the effects of orientation of the molecules under the influence of an applied electric field according to Debye's theory, the maximum power factor occurring when the period of the applied voltage bears a definite relation to the relaxation time of the molecules, which is determined by their effective radius and the viscosity of the material. The effective radius of the molecules, calculated from observed values of viscosity and relaxation time, is in every case of the same order as the radius of the OH group obtained from x-ray measurements. It is therefore believed that the dielectric behaviour of resins of this type is mainly determined by the rotation of the OH groups in their molecules. The only important differences between the electrical properties of the phenol, cresol and xylenol thermoplastics are those associated with differences of viscosity.

§1. INTRODUCTION

As one object of this paper is to open a discussion on plastics between physicists and industrial chemists, it will be well to consider briefly the general problem, as well as the particular one with which our own experiments are concerned. From the ordinary common-sense point of view, plastics are materials suitable for the processes of the moulding trade. From the scientific point of view a plastic is not just a material produced to meet the requirements of any particular industrial process, but simply an organic material with a large molecule. The plastic chemist's job is essentially the building up of such molecules from simpler ones, and the great importance of the process lies in the

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vast scope which it offers for obtaining any desired combination of properties, e.g. great mechanical strength combined with lightness, and the power of absorbing mechanical vibrations; or good insulating properties combined with flexibility; and so on. The large molecular structures are capable of so many variations that the possibilities are endless. Before they can be realized, however, much work must be done on the relation between the properties of plastics and their structure, work for both chemist and physicist.

It may be recalled that plastics, broadly speaking, fall into two classes: (*a*) the thermoplastics, which soften on heating, and solidify again on cooling, the process being reversible, and (*b*) the heat-hardening or thermo-setting resins, which soften on first heating, but solidify again on continued heating, the latter process being irreversible. The thermoplastics are the materials with molecules consisting of long chains: the thermo-setting resins are those with molecules of a girder-like structure; and it is believed that the process of heat-hardening consists of the cross-linking of chain molecules into a girder structure. Thermoplastics are largely soluble in organic liquids. The solvent molecules apparently have little difficulty in forcing their way between the chain molecules, but cross-linking tends to prevent such action. A material with molecules that are partially cross-linked may swell but not dissolve in a liquid, while complete cross-linking may enable a material to resist the action of liquids completely. These are some of the simplest ways in which properties depend on molecular structure, and the extension of such knowledge is the main object of the scientific study of plastics.

Our own investigation is a contribution to the study of dielectric properties, and forms the second part of a comprehensive investigation carried out on behalf of the British Electrical and Allied Industries Research Association. The first part[1], dealing with the heat-hardening phenolic resins, was discussed on a previous occasion. This paper deals with the corresponding thermoplastics.

§ 2. THE MATERIALS

The materials examined included a series of resins made by condensing formaldehyde with phenol, *o*-, *m*- and *p*-cresol, and *m*-5-xylenol; and also a resin prepared by Dr. D. V. N. Hardy from benzyl alcohol.

The phenol-formaldehyde resin was made as follows:—A solution made by mixing 376 g. phenol (4 g. mols), with 225 ml. of 40 per cent formalin (3 g. mols) and 0·5 ml. of 2N-hydrochloric acid to serve as catalyst, was heated in a bath of boiling water until the liquid became turbid, on account of the production of particles of resin by the condensation reaction. The time required was about 2 hours. The mixture was then cooled, the top aqueous layer decanted, and the remaining resin washed five times with a litre of boiling water in order to remove the acid. The final washings having been found to be free from acid, the remaining water was removed by distillation. The resin was finally distilled under a pressure of about 18 mm. Hg up to a temperature of about 130° c. to remove uncombined phenol. The yield of resin was about 240 g.

The preparation of the other phenolic resins was on similar lines, 4 g. mols of the cresol or xylenol being condensed in each case with 3 g. mols formaldehyde, using sufficient catalyst (usually 0·5 to 1·0 ml. of 2N-HCl) to produce turbidity in a convenient time.

One sample, after being prepared as described above, was subjected to further distillation at a higher temperature in order to remove dihydroxydiphenylmethanes. Care was taken to avoid decomposition, which would result in a heat-hardening of the resin. The distillation occurred mainly at 225° c. and 5 mm. Hg, but was cautiously continued up to 234° c., 15 mm. Hg. The quantities of phenol, formalin, etc., used were 3/4 of those first mentioned: the yield of resin was about 148 g., and about 33 g. of dihydroxydiphenylmethanes was removed. This resin had a softening point of about 76° c., as against 61° c. for the corresponding one made without this final distillation.

The benzyl alcohol resin was prepared by Dr. D. V. N. Hardy in connection with experiments on the synthesis of acids from alcohols by high-pressure treatment with carbon monoxide[2]. Resins of this type have been produced simply by heating benzyl alcohol with phosphoric acid (cf. British Patent 269973). In the present instance benzyl alcohol vapour, admixed with steam and carbon monoxide under a pressure of 150 atmospheres, was passed through phosphoric acid at 300° c. After cooling, the phosphoric acid was found to be covered with a solid block of yellowish-brown resin. This resin was dissolved in benzene, and the solution was repeatedly shaken with considerable quantities of water to remove the phosphoric acid. The benzene was then removed by heating, firstly under atmospheric pressure in a water-bath, and secondly under reduced pressure in an oil bath at 200° c. The resulting resin had a molecular weight of 625 (cryoscopic from benzene), which corresponds roughly with the molecular weight of the phenolic thermoplastics.

§ 3. MEASUREMENTS

The experiments made with these resins included measurements of permittivity, ϵ (dielectric constant), and loss tangent, tan δ, over a considerable range of temperature, using alternating current of frequency from 300 to 7 000 c./s.; measurements of the coefficients of viscosity of the resins as far as possible covering the same range of temperature; and measurements of the direct-current resistivity of one typical resin.

The technique employed calls for little comment. The electrodes used for the electrical measurements consisted of two lengths of pure nickel tubing, with an annular gap of about 3 mm. between them, the arrangement forming a cylindrical condenser of length 10 cm. and overall diameter 2·5 cm. Three small wedges of fused quartz inserted into the annular gap at each end of the condenser served to make the structure rigid without affecting its capacitance or power factor to any significant extent. The capacitance of the condenser in air having been measured, the resin was melted in a boiling tube, and the condenser, previously

heated to about the same temperature, was lowered into the molten resin until it was completely immersed, except for two narrow strips of nickel provided with terminals, which served to make connection with the measuring apparatus. The resin was maintained in a molten condition until all air bubbles had escaped: it was then allowed to cool.

At first nickel tubes providing a gap of about 1 mm. were employed, but the forces brought into play during the setting of the resin on cooling caused the rather thin quartz wedges to fracture, and stouter wedges necessitating a gap of 3 mm. had to be used. The boiling tubes were also liable to be fractured in the same way, especially by the phenol resin, and stout tubing (in some cases "Monax") became necessary.

The capacitance and power factor of the resin-filled condenser were measured by means of a Schering bridge. A Wagner earth-connection was employed, a screen of tinfoil wrapped round the boiling tube being connected to earth, so that the glass tube and other neighbouring objects could have no effect on the measured capacitance and power factor. Measurements on the condenser when empty showed that the contribution of the quartz wedges to the power factor was negligible. Their capacitance, and that of the nickel strips and terminals, were appreciable, but small enough to justify their being neglected when considering relative values of permittivity. The ratio of the measured capacitance of the resin-filled condenser to that of the same condenser in air was therefore taken as the permittivity of the resin, while its power factor is that of the filled condenser.

The measurements of d.c. resistivity were made with the same condenser, the tinfoil screen serving as a guard-electrode. This does not of course guard against the conduction current through the quartz wedges, but this current was very small compared with that through the resin itself, and was therefore ignored. The current flowing on the application of 200 volts to the electrodes was measured by means of a sensitive galvanometer. The current diminished somewhat with the time during which the voltage was applied, i.e. there was some absorption. The value taken was that flowing about 3 seconds after the application of the voltage.

The measurements of viscosity were made by means of the modified Ostwald viscometer described by Lee[3] for measurements on tars.

§ 4. VALUES OF PERMITTIVITY AND LOSS TANGENT

Typical curves showing values of permittivity (or dielectric constant) and loss tangent for the various resins are given in figures 1, 2 and 3. Referring to figure 1, which shows tan δ, plotted for convenience on a logarithmic scale, against temperature on a uniform scale, it will be noted that the loss tangents of the phenolic thermoplastics at ordinary temperatures, when the resins are in the solid state, are of the same order as that of the corresponding heat-hardened resin in the dried condition. The values of permittivity are also approximately the same for heat-hardened and thermoplastic resins in these conditions, as may be seen in

figure 2. But while the values of both loss tangent and permittivity for the heat-hardened resin are comparatively unaffected by a change of temperature, the loss tangent of all the phenolic thermoplastics rises to a very high maximum value at a temperature which varies with the chemical composition of the resin, and, as will be seen later, with the frequency. Corresponding to the maximum value of tan δ there is an increase of permittivity with rise of temperature which is shown in figure 2. It may be noted that the permittivity increases most rapidly with temperature in the region of temperature in which the power factor passes through its peak value.

The behaviour of the benzyl alcohol resin is very similar to that of the phenolics,

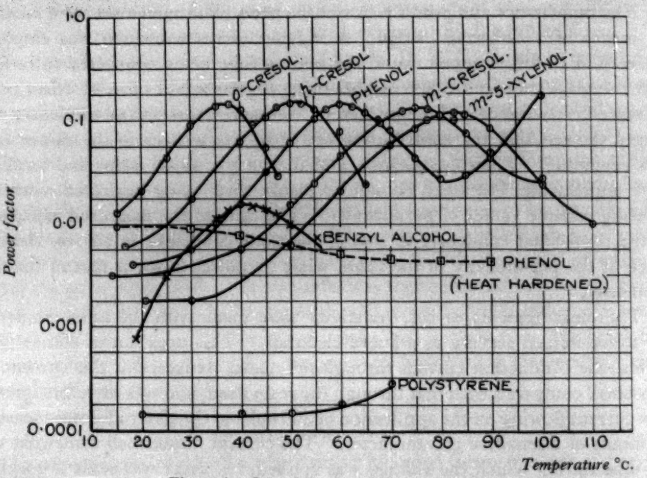

Figure 1. Power factor-temperature curves.

but the changes of permittivity and all the values of loss tangent are of a lower order for this resin than for the phenolics.

Values obtained for a sample of a thermoplastic hydrocarbon resin, polystyrene, are also shown for comparison. For this material the power factor is of a still lower order, and there is little suggestion of a maximum value. Materials of this type are of interest in showing how near to the perfect dielectric a thermoplastic can approach.

Referring to figure 1, it is interesting to note that in proceeding from the phenol to the *m*-cresol and *m*-5-xylenol resins, the curve for tan δ is merely shifted along the temperature axis, other changes being comparatively small, although it may be noted that the effect of the additional methyl groups in the *m*-cresol and *m*-5-xylenol resins is to reduce the power factor slightly, a result

which corresponds closely with that previously obtained for the heat-hardened resin.

It will be observed that the *o*- and *p*-cresols have rather higher maximum loss tangents than the *m*-cresol resin. It is thought that this indicates the existence of some cross-linking in the *m*-cresol resin. The phenol and *m*-cresol molecules may both take part in the formation of cross-linked molecular structures, since there are three reactive points on each of these molecules, two ortho and one para. In the *o*- and *p*-cresols one of the three points is no longer reactive, and these molecules can therefore only form chain structures. It is to be expected that any cross-linking will reduce the maximum loss tangent, since the heat-hardened material, i.e. the completely cross-linked structure, showed no such maximum.

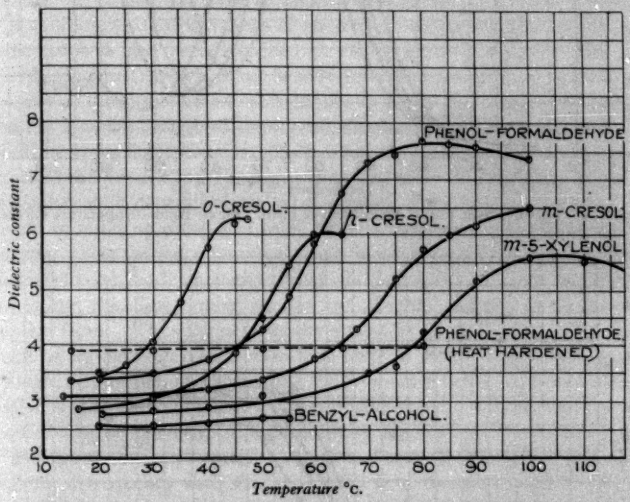

Figure 2. Thermoplastic resins. Dielectric constant-temperature curves.

The curves of figures 1 and 2 were obtained at a constant frequency of 1 000 c./s. Similar measurements were made on all the resins at various frequencies covering the range 300 to 7 000 c./s. The curves were in every case very similar to those of figures 1 and 2, and it is not considered necessary to reproduce them all. Those of figures 3 and 4 may be taken as representative. In figures 3 and 4 it will be observed that an increase of frequency merely shifts the curves along the temperature axis, without appreciably altering either the maximum value of tan δ or the upper and lower (more or less) stationary values of permittivity. Another point to be noticed in figure 3 is that, as the temperature is increased beyond the point at which tan δ reaches its maximum value, the rapid diminution of value is

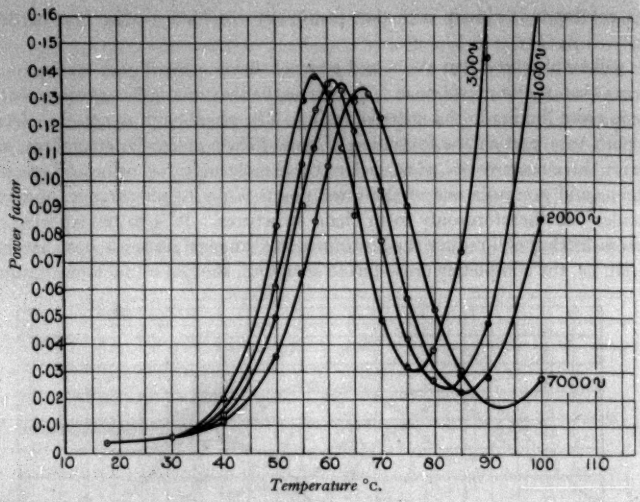

Figure 3. Thermoplastic phenol-formaldehyde resin. Power factor-temperature curves.

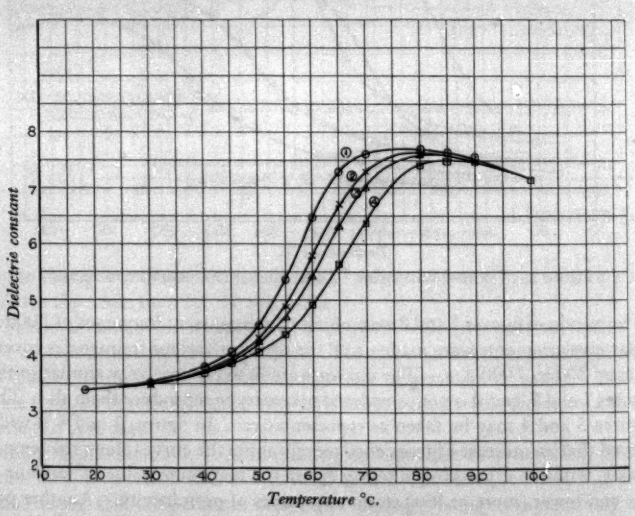

Figure 4. Thermoplastic phenol-formaldehyde resin. Dielectric constant-temperature curves.
(1) 300~ (2) 1000~ (3) 2000~ (4) 7000~

followed by an equally rapid increase. These high values of tan δ in the region beyond the first peak were found to vary inversely as the frequency, which shows that in this region the material has acquired a conductivity which is approximately independent of frequency, and is therefore probably normal ionic conductivity.

The values of ϵ and tan δ at a constant temperature were also plotted against frequency, and curves somewhat similar to those for varying temperatures and constant frequency were obtained, i.e. tan δ passes through a high maximum value at a certain frequency, which depends on the temperature, and there is a relatively rapid fall in the value of permittivity as the frequency increases through a small range in the region of maximum tan δ.

§ 5. THE RELAXATION TIME

It is well known that variations of dielectric constant and loss tangent with frequency such as have been described are characteristic of a polarization, or an electric displacement which is not wholly instantaneous in its action : i.e., a component of the displacement only builds up to its final value if the force is applied for a certain length of time; and, similarly, when the applied force is removed an appreciable time is required for the displacement to disappear. When, as in the present experiments, the applied force is alternating, the extent of the displacement depends on the relative values of the time required for a displacement to build up to its final value under a constant applied force, and the time during which the force continues to act in one direction, i.e., the half-period, which depends on the frequency. When the period is very large, i.e., the frequency is low, the displacement reaches its full value, and also keeps pace with the applied force. Thus the permittivity attains its upper limiting value, and δ, the angle of lag between displacement and force, is zero. When the frequency is very high, i.e., the period is very small, the component of the displacement under discussion is unable to build up to any appreciable extent ; only the instantaneous component can be operative, the permittivity reaches its lower limiting value (the " instantaneous " or " optical " value), and again δ, the angle of lag, is zero. For values of frequency such that the period is of the same order as the time required for the displacement to build up, the permittivity has an intermediate value, and the displacement lags more or less behind the applied force, δ. Tan δ passes through a maximum value for a certain value of the frequency in this region.

The simplest case, mathematically, is that in which the building-up and the decay of the displacement (or that component of the total which is not instantaneous), follows an exponential law, the decay being expressible in the form $D = D_0 e^{-t/\tau}$, where D represents the displacement at a time t measured from the instant at which the applied force is reduced to zero, D_0 is the value of the polarization at this instant, and τ is a constant characteristic of the retarded displacement, viz., its relaxation time, or the time required for it to decay to $1/e$ of its initial value. For a displacement which consists simply of an " instantaneous " component

and a retarded component of this kind, the variation of permittivity ϵ, and tan δ, with frequency $\omega/2\pi$ are given by[4]

$$\epsilon = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1+\omega^2\tau^2} \qquad \ldots\ldots(1)$$

and

$$\tan\delta = \frac{(\epsilon_0 - \epsilon_\infty)\omega\tau}{\epsilon_0 + \epsilon_\infty\omega^2\tau^2}, \qquad \ldots\ldots(2)$$

where ϵ_0 and ϵ_∞ are the two stationary values of the permittivity, the optical or instantaneous value ϵ_∞, and the static or zero-frequency value ϵ_0. Equation (2) shows that tan δ reaches a maximum value at the angular frequency ω_m, where

$$\omega_m\tau = \sqrt{(\epsilon_0/\epsilon_\infty)}, \qquad \ldots\ldots(3)$$

and that the maximum value tan δ_m is given by

$$\tan\delta_m = \frac{\epsilon_0 - \epsilon_\infty}{2\sqrt{\epsilon_0\epsilon_\infty}}. \qquad \ldots\ldots(4)$$

It should be stated here that although the experimental curves are of the same general character as those of equations (1) and (2), the agreement is not very close. The observed maximum value of tan δ is, for example, considerably less than that obtained by substituting the two stationary values of ϵ in (4). Nevertheless, the peak in the curve of tan δ is sufficiently pronounced to leave no doubt that the materials are characterized by a time of relaxation τ the order of which can be obtained by substituting in equation (3) the value of frequency $\omega_m/2\pi$, at which tan δ reaches its maximum value. The relaxation times of the material at various temperatures were determined approximately in this way.

§ 6. THE MOLECULAR RADIUS

There are many possible types of displacement or of polarization characterized by a relaxation time of this character. It is only necessary that the motion of the displaced charges shall be opposed by an " electric force " proportional to their displacement, and a frictional or viscous force proportional to their velocity, but in seeking for an explanation of our observations it is natural to turn to Debye's theory of the polarization produced by the orientation of molecular dipoles under the influence of an applied electric field. Figure 5 shows clearly that the maximum value of tan δ for a series of similar resins varies directly as the proportion of polar groups in the molecule, and the upper limiting value of the dielectric constant is a linear function of the same quantity. These facts alone provide a strong indication that the properties observed are closely connected with the polar structure of the molecules. Making a tentative assumption that the molecule can be treated as a small sphere, the rotation of which is retarded by the viscosity of the surrounding medium, Debye[5] obtained for the relaxation time (τ') of the polar molecules in terms of the coefficient of viscosity (η) and the radius of the sphere (a)

$$\tau' = \frac{4\pi\eta a^3}{kT}, \qquad \ldots\ldots(5)$$

where k is Boltzmann's constant and T is the absolute temperature. The time of relaxation τ in equations (1) to (3) is not in general the same as τ' in (5), since τ is the value characteristic of the dielectric constant, while τ' is the relaxation time for the polarizable units, or the polarizability of the material. Thus τ is defined by reference to the displacement and the applied electric field, while τ' refers to the polarization and the internal field. The relation between the two

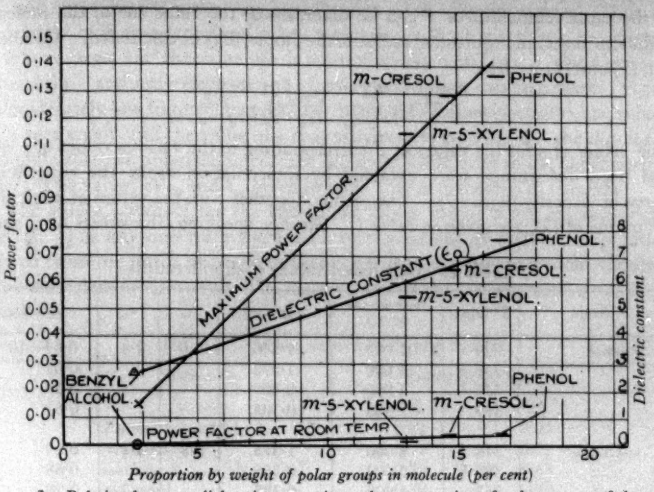

Figure 5. Relation between dielectric properties and concentration of polar groups of thermoplastic resins.

Note.—Since the paper was written Dr. Hardy has analysed the benzyl alcohol resin and obtained the result:—C=91·75, H=6·68, and therefore O is about 1·5 per cent. The formula assumed in the paper, viz., $C_6H_5.CH_2[C_6H_4.CH_2]_6.OH$, corresponds to C=89·90, H=7·64, O=2·46 per cent, and it follows that only 60 per cent of the resin molecules are hydroxylated, and that the value we have assumed for the proportions of polar groups in the molecule of this resin should be reduced by 40 per cent. If this is done it will be seen that the curve for maximum power factor in figure 5 passes through the origin, which adds further support to the view we have put forward. The effect on the curve of dielectric constant is comparatively small; the intercept on the ϵ axis becomes 2·0 instead of 1·7. Probably the new value is a little closer to the square of the refractive index of these materials, but in any case our main conclusions are unaffected.

Dr. Hardy has pointed out that the low hydrogen-content of his resin shows that about six atoms of hydrogen have been eliminated per molecule, and since small quantities of anthracene and dihydroanthracene were obtained during the reaction, he concludes that the hydrocarbon constituent of the resin contains an anthracene grouping. Rings other than those of the original benzyl alcohol, e. g., of 5 and 6 carbon atoms, must be produced by the direct elimination of hydrogen. There must be, on the average, three additional rings per molecule of resin.

quantities is not precisely known for materials of the kind under consideration. For gases $\tau=\tau'$, while for materials which obey the Clausius-Mosotti relation, we have

$$\tau=\frac{\epsilon_0+2}{\epsilon_\infty+2}.\tau', \qquad \ldots\ldots(6)$$

the equation given by Debye. The maximum value of $(\epsilon_0+2)/(\epsilon_\infty+2)$ for the materials investigated is 1·8, so that the uncertainty in the ratio τ/τ' is not likely to be of great importance in a preliminary examination of the problem. As a first approximation equation (6) was adopted, and the values of τ' at various temperatures T obtained from the corresponding values of τ. Referring now to equation (5) it is obvious that if the coefficient of viscosity η for the material at the same temperatures T can be determined, the value for a, the molecular radius, or rather the equivalent radius of the dipole, may be calculated. Combining (3), (5) and (6) we have

$$a^3 = \frac{kT}{4\pi\eta\omega_m} \cdot \frac{(\epsilon_\infty+2)}{(\epsilon_0+2)} \cdot \sqrt{\frac{\epsilon_0}{\epsilon_\infty}}. \qquad \ldots\ldots(7)$$

The values of η for the values of T corresponding to the various values of τ which had been determined were obtained by interpolation from the experimental curve of viscosity (figure 7). The results, together with the values of a calculated by means of (7), are given in table 1. Strictly speaking, the values of ϵ_0 and ϵ_∞

Table 1. Calculated values of dipole radius

Resin	$T°$ (abs.)	$f_m = \omega_m/2\pi$ (c./s.)	η (poise)	ϵ_0	ϵ_∞	a (cm.)
Phenol	334	1 000	1·846	7·6	3·4	$0{\cdot}64\times10^{-8}$
	335·5	2 000	1·072			0·61
	337	4 000	0·609			0·59
	339	7 000	0·308			0·61
m-Cresol	348·5	1 000	1·578	6·5	3·1	0·69
	350·5	2 000	0·855			0·68
	353	4 000	0·385			0·70
	355·5	7 000	0·190			0·74
m-5-Xylenol	353·5	500	0·640	5·6	2·8	1·20
	355	1 000	0·406			1·11
	357·5	2 000	0·202			1·11
	360	4 000	0·090			1·16
	362	7 000	0·050			1·12
o-Cresol	311·5	2 000	0·495	6·3	3·3	0·79
	313	4 000	0·290			0·76
	314·5	7 000	0·172			0·75
p-Cresol	324	1 000	1·000	6·0	2·9	0·78
	326	2 000	0·460			0·81
	328	4 000	0·285			0·76
	330	7 000	0·148			0·79
Benzyl alcohol	301·5	300	0·880	2·70	2·58	1·27
	312	500	0·500			1·29
	314·5	1 000	0·195			1·41
	317·5	2 000	0·093			1·43

could only be obtained from measurements made over an extremely wide range of frequencies at the temperature T. An estimate of the values is, however, more easily obtained from measurements covering a wide range of temperature and a moderate range of frequency. The results given in figures 3 and 4 considered in relation to equations (1) and (2) show that ϵ_0 and ϵ_∞ vary but little with temperature. On the other hand equation (5) shows that τ' is proportional to η/T, and therefore increases very rapidly with a fall in temperature. Thus at a moderately high frequency and a low temperature (high viscosity), the value of $\omega\tau$ is very large, and the value of ϵ is approximately equal to ϵ_∞: the dipoles are " frozen in " and only electron and atomic polarization can take place. Again, at a moderately low frequency and a high temperature (low viscosity), the value of $\omega\tau$ is very small, and the value of ϵ is approximately equal to ϵ_0: the dipoles are so mobile that the polarization reaches the static value even in the short periodic time. The values of ϵ_0 and ϵ_∞ given in table 1 were estimated in this way.

The values obtained for the equivalent dipole radius a are of considerable interest. For any one resin the values corresponding to various temperatures differed from the mean by no more than 5 per cent, in spite of tenfold variations in the coefficient of viscosity. The mean values for the various resins are collected in table 2.

Table 2. Mean values of dipole radius

Resin	Radius (in 10^{-8} cm.)	
	(1)	(2)
Phenol-formaldehyde	0·61	0·74
o-Cresol- ,,	0·77	0·89
m-Cresol- ,,	0·70	0·83
p-Cresol ,,	0·78	0·92
m-5-Xylenol formaldehyde	1·15	1·34
Benzyl alcohol	1·35	1·36
OH group (x-ray value)	1·5	

§7. DISCUSSION OF RESULTS

It is recognized that these values can be regarded as no more than an approximate estimate of the equivalent radius of the dipoles, for it has already been mentioned that the simple equations (1) and (2) are not accurately obeyed. For example, equation (2) can be expressed in the form

$$\frac{\tan\delta}{\tan\delta_m} = \frac{2\omega/\omega_m}{1+(\omega/\omega_m)^2}, \qquad \ldots\ldots(8)$$

from which it is clear that if the ratio of the loss tangent to its maximum value is plotted against the ratio of the frequency to the value corresponding to the maximum loss tangent, a curve of characteristic shape should be obtained, whatever the material. Note that the value of $\tan\delta/\tan\delta_m$ given by this equation is the same for $\omega/\omega_m = x$ and $\omega/\omega_m = 1/x$, so that if this curve is plotted with a logarithmic scale for the frequency ratio the curve is symmetrical about the ordinate through

the point $\omega/\omega_m = 1$, as shown in figure 6. Curves (1) and (2) represent the experimental values for two of our resins, while the lowest curve is that representing equation (8). The peaks in the experimental curves are much blunter than that of the theoretical one. The blunt peak may be regarded as the resultant of a number of neighbouring peaks of the theoretical form superposed, which would mean that the material is characterized, not by a single relaxation time, but by a band of such times, the sharpness of the experimental peak providing some indication of the width of the band. The suggestion of the existence of groups or bands of relaxation times has been made by several previous ob-

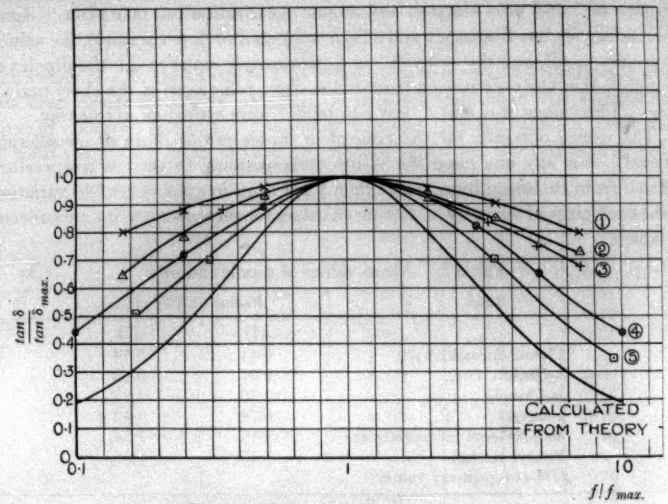

Figure 6. Power factor-frequency curves.

(1) Phenolic resins (authors).
(2) Benzyl alcohol resin (authors).
(3) Rubber-sulphur compounds (Scott, McPherson and Curtis).
(4) Cetyl palmitate in paraffin wax (Sillars).
(5) Chlorinated diphenyl (Jackson).

servers[6], and it seemed worth while to examine the existing published data to find out to what extent the curves obtained for different materials varied from one another. Unfortunately, very few observers have made measurements at a number of frequencies sufficient to define such a curve, but curves (3), (4) and (5) in figure 6 were plotted from data published for ebonite[7], a solution of a polar ester in paraffin wax,[8] and chlorinated diphenyl[9] respectively. There are considerable differences between the curves for the various materials, but the relation between the relative widths of the peaks and structure of the materials is by no means obvious. The curves suggest that the band of relaxation times

for these resins is wider than that for several comparable materials, and single values such as those which we have obtained must therefore be used with caution. The general consistency of the results does, however, suggest that the values of a represent at least the order of magnitude of the radius of the dipoles.

The smallness of these values is one of their most striking features. The value for the radius of the OH group determined by x-ray methods is given in table 2 for purposes of comparison, and it may be seen that the value obtained for the dipole radius of two of the resins is practically the same as the radius of the OH group, while the others are rather smaller. It is clearly impossible that the

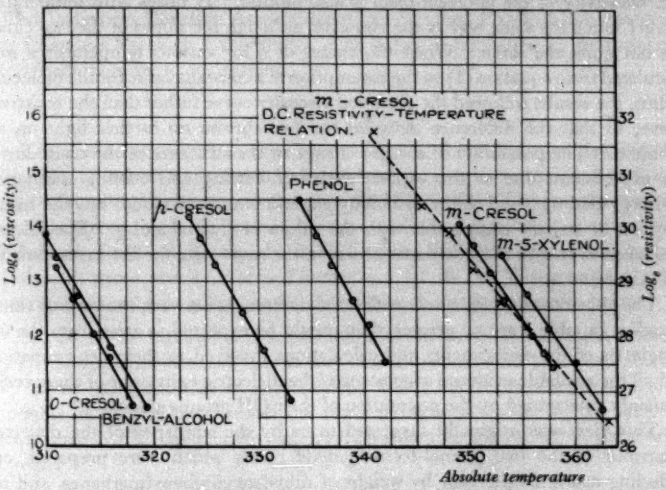

Figure 7. Relation between viscosity and temperature.

effective radius of rotation of these large molecules should be less than that of a single OH group, but since each of the resins is known to contain the OH group in its molecule, it seems most probable that it is these groups alone that suffer orientation by an electric field, and that the differences from the value $1{\cdot}5\times 10^{-8}$ cm. represent the errors involved in the various assumptions made. It is to be remarked that the curve of figure 6 for the benzyl alcohol resin is closer to the theoretical curve than those of the phenolic resins, and it is significant that this resin gives a value for the radius very near to that of the OH group. Another interesting point arises in connection with the use of equation (6), which, as previously mentioned, corresponds to the assumptions of the Clausius-Mosotti relation. It has been maintained[10] that this relation is not applicable to highly polar materials, and for liquids like water an empirical relation corresponding to the relation $\tau=\tau'$ instead of (6) has been proposed. In table 2 the

column headed (1) gives the mean values taken from table 1, and that headed (2) gives the values obtained if the relation $\tau = \tau'$ is used instead of (6). The low values are brought considerably nearer to that of the OH group, while the value for the benzyl alcohol is practically unaffected.

A further point for consideration is the application of values of the coefficient of macroscopic viscosity to the motion of single molecules, and still more to parts of molecules. A similar assumption is often made when considering the mobility of ions, which is a factor determining the resistivity of materials. In figure 7 the macroscopic coefficient of viscosity is plotted as a function of temperature. The d.c. resistivity of the *m*-cresol resin is also plotted. It varies with temperature in very much the same way as the viscosity, although the slopes of the two curves are not quite the same. When the values of η for various temperatures were calculated from equation (5) on the assumption of a constant value for the molecular radius, the results followed the observed viscosity curve rather than the resistivity curve, so that the difference between the two throws no further light on the problem. The possibility of a slight change in the structure of the resin during the experiment, due to the various cycles of heating and cooling, cannot be entirely ruled out, and as the resistivity experiments were made last, the results may not be strictly comparable with the values of ϵ, $\tan\delta$ and η. Special care was taken to ensure that the material was in the same state for the measurements of ϵ, $\tan\delta$ and η.

The above considerations show that the differences between the various values of radius in table 2 are no greater than might be expected to arise from the uncertainties of the experiments and calculations involved in their determination, and all the available evidence suggests that the dielectric behaviour of these resins is mainly determined by the orientation of their OH groups alone.

This view was originally suggested to us by the similarity of the dielectric behaviour of the two phenol-formaldehyde resins which were prepared, one including nearly 20 per cent by weight of dihydroxydiphenylmethanes, and the other being comparatively free from these compounds. Each of these resins gave curves of $\tan\delta$ and ϵ similar to those of figures 1 to 4. The maximum values of $\tan\delta$ and ϵ were smaller for the resins from which the dihydroxydiphenylmethanes were removed, and the peak in corresponding curves of $\tan\delta$ occurred at a higher temperature, corresponding to the greater viscosity of this resin at the same temperature, but otherwise the curves were similar, leading to the conclusion that the contribution of the comparatively small molecules of the dihydroxydiphenylmethanes to the dielectric behaviour of the resins was essentially similar to that of the larger chain molecules, and that therefore both were likely to be due to some feature common to the two molecules, i.e., the OH group. It was this observation which prompted the investigation of the equivalent radius of rotation of the series of resins, and the comparison of the estimated values with the x-ray value for the OH group.

From the work of other experimenters[11] it appears that certain polar molecules,

consisting of chains of the paraffin type, when dissolved in paraffin wax rotate as rigid rods about their long axes. Such a rotation might also be expected to give a small equivalent radius for a comparatively large molecule, but the present investigation suggests that for the series of resins examined it is more probable that the dielectric behaviour is determined by the rotation of the OH groups independently of any motion of the molecule as a whole.

§ 8. ACKNOWLEDGEMENTS

This work forms part of a comprehensive investigation of the dielectric properties of synthetic resins carried out on behalf of the British Electrical and Allied Industries Research Association at the National Physical Laboratory and the Chemical Research Laboratory. The paper is published by permission of the Directors of these institutions.

DISCUSSION

The discussion, which was not confined to the electrical properties, but dealt also with chemical and mechanical problems, is not here reprinted in full; it may be found in *Chemistry and Industry*, **59**, 537 (1940). The contributors were Drs. W. Blakey, N. A. de Bruyne, Messrs. G. G. Burleigh, H. L. Cox and W. J. O'Doherty, Dr. F. C. Frank, Mr. B. C. Fleming-Williams, Prof. Willis Jackson, Messrs. E. Stern and A. Morris Thomas and Dr. W. G. Wearmouth, of whose contributions only the parts bearing directly on this paper are given below.

Dr. N. A. DE BRUYNE. Is it possible that the times of relaxation measured by Dr. Hartshorn electrically are in any way connected with those computed by W. Kuhn (*Z. phys. Chem.* 1939 (B) **42**, 1–38), on the assumption that the modulus of rigidity of all materials, whether liquid or solid, are the same—an assumption which has recently received considerable support from the work of Raman?

Mr. G. G. BURLEIGH. In testing phenolic resins for ultimate tensile strength, I have observed a not very marked yield point in the region of 1500 lb./in.^{2}, and a much more marked yield point at about 2500 lb./in.^{2} At stresses above 4000 lb./in.^{2} the materials yield continuously as the stress is increased.

Mr. B. C. FLEMING-WILLIAMS. There is reason to believe that when a plastic is mechanically stressed, there is first an instantaneous yield, secondly a yield requiring many minutes or even longer to become complete, and thirdly, if the stress is great enough, a continuous flow of the material. The second effect may be partially elastic, the strain slowly relaxing if the stress is removed.

Under these circumstances it would seem that the ordinary methods of mechanical testing of plastics, developed from those used on metals, do not give sufficient data for the behaviour of the plastic to be deduced under circumstances other than those of the actual test. For instance, a figure may be given for Young's modulus of the material, but actually for a plastic this " constant " would vary

with the magnitude of the stress, the time of application of the stress and the temperature. This also applies to other constants such as impact strength, compressive strength, etc. Some indication of the magnitude of these variations would have to be given before the behaviour of a plastic under a given set of conditions could be deduced. If additional data of this type were given then the actual properties of the material would be more nearly described.

At the very least, the constants of a plastic should be expressed in a form taking cognisance of the time factor.

Dr. F. C. FRANK. There are three aspects of the usefulness of such work as that presented to us by Dr. Hartshorn. Firstly, and obviously, the direct use of measurements by the engineer in choosing from known materials for a given purpose. Secondly, in the guidance of the chemist who wishes to foresee the properties of hypothetical plastics or to attempt to make plastics with required properties. From this aspect a fairly satisfactory stage has been reached: of course, conflicting properties are often specified (for example, low dielectric loss and great strength), and thought and trial are still required to effect the best compromise, but the search need no longer be made blindly. In the third aspect, measurements may be used to study the inner molecular mechanics of a material to give information which ultimately serves our second aspect.

1. *The relaxation time* τ at a given temperature is found from the frequency of maximum loss. The molecular motions are probably well represented as very high-frequency oscillations (say 10^{12} c./sec.) with less frequent large random changes of orientation, in which case τ is the mean time between successive large changes. Thus at that temperature at which the substance has maximum loss for 10^8 c./sec., each polar group makes something of the order of 10^8 spontaneous jumps in orientation every second. This occurs all the time, whether a field is applied or no. From this point of view viscosity and τ are related because molecular motions determine viscosity, rather than conversely.

2. *The variability of* τ is indicated by the extent to which the loss curve is wider than the ideal form given by Debye's theory. An abnormally wide curve may indicate the presence of specific forces between molecules, since in the absence of such forces only the space-filling in the environment of each polar group determines its freedom: specific forces between certain atoms add another variable quantity (butylphthalate in polystyrene * is a possible example).

3. The temperature coefficient of τ yields by comparison with an equation of Arrhenius's form,

$$1/\tau = Ce^{-A/RT},$$

an activation energy A, being the excess energy required as a thermal fluctuation to loosen up the environment of a polar group to enable it to change direction.

* Frank and Jackson, *Trans. Faraday Soc.*, March 1940.

4. *The activation frequency C* in this equation can be related to the extent of the region which is loosened up in the average activation process. If the polar group behaved as a single vibrator in a static environment, *C* would be a molecular vibration frequency of, say, 10^{12} to 10^{13}, but if a variety of combined local vibrations can permit rotation, *C* will have a very much larger value.

5. The total change of dielectric constant through the dispersion range (or a suitable integral of dielectric loss) is often equivalent to the number and magnitude of dipoles present according to Debye's formula for free molecules (e.g., in vulcanized rubber as shown by H. Muller). When it falls off from this value, we learn that *elastic restrictions* as well as viscous ones play a part. In terms of the simplest possible model, in which there are two opposed orientations of each dipole at minima of potential energy, separated by a potential barrier of height *A*, this falling off can be related to another energy difference *U*, the difference between the two minima. No unambiguous analysis of such data is yet possible, and theories have to be disentangled, but those of Debye and Onsager are not such flat contradictions as at first they seem.

Prof. WILLIS JACKSON. While it is natural for the electrical engineer to have a special interest in the electrical properties of new materials, it is, nevertheless, a fact that the properties about which his first pointed enquiries will be made are the physical and mechanical ones, though different engineers will cite different properties as of most importance. Thus one will stress the need for materials of higher softening " points ", another for greater impact strength, improved moisture-sealing properties, freedom from hot-oil attack, higher resistance to surface " tracking ", and so on. Improvements in electrical properties are unlikely to arouse interest unless linked with improvements of a physical or mechanical nature. The electrical engineer has already available a number of materials of excellent electrical properties—polystyrene and Polythene are recent examples—for which only a limited application has been found because of deficiencies in the above respects. The time is fully ripe for the development of more scientific methods for studying physical and mechanical properties generally, so that a more satisfactory basis may be provided for explaining them as they arise in existing dielectric materials and for forecasting them for new ones.

The difficulty which obstructs a fuller understanding of the mechanisms underlying the electrical and mechanical behaviour of amorphous solids is our lack of knowledge of the forces restricting the relative motion of the constituent molecules and, in particular, of a polar group relative to its parent, or to an adjacent, molecule. This lack of knowledge is usually glossed over by reference to an internal viscosity, the physical significance of which is uncertain. It seems that purely electrical measurements can give only a limited insight into this matter and that co-ordinated measurements of the mechanical damping of materials offer the most promising alternative line of attack: have any co-ordinated electrical and mechanical measurements been carried out on these lines?

The need for the synthesis of three-dimensional molecules, cross-linked with primary bonds and free from condensation products, of which water is the most undesirable, has frequently been mentioned.

Mr. A. Morris Thomas. The electric strength of insulants as determined by the usual industrial methods of test and as revealed in service is dependent almost entirely on extraneous influences (e.g., discharges in the ambient medium or in internal voids, or by weak spots or defects in the material). Nevertheless, there is a property termed the *intrinsic electric strength* which depends only on the structure and certain physical constants of the material itself.

Although it may not be possible at this stage to state definitely that investigation of the intrinsic electric strength of plastics will further our understanding of their structure, yet certain results have been obtained which may be related thereto.

Recently a theory of electrical breakdown applicable to polar crystals has been developed which has enabled a quantitative comparison with experimental results to be made, and good agreement has been obtained. According to this theory there should be an increase of intrinsic electric strength with temperature at temperatures below the thermal breakdown region.

It was therefore of some interest to ascertain if this temperature dependence was shown by varnish films. Intrinsic electric strength tests down to $-196°$ c. (temperature of liquid nitrogen) were made on natural resin films (including shellac) and synthetic resin films of the bakelite type. It was found that all these substances at $-196°$ c. have the remarkably high intrinsic electric strength of between 8000 and 9000 kv./cm., which is approximately the same as that of muscovite mica at this temperature. The mica, however, shows the small increase with temperature up to 0° c. predicted by the theory, but the varnish films give an almost linear decrease which is rather more rapid with the natural than with the synthetic resins, so that at 0° c. the values are about 3500 kv./cm. for the former and 4500 kv./cm. for the latter. Above about 20° c. and up to 80° c. there is a tendency for the values to become constant except that shellac films give a rapid decrease at 60° c.

The thickness of the films tested ranged from 5 to 50 microns. Polystyrene and polyethylene have also been tested at room temperatures, and both are found to possess an intrinsic electric strength as high as 5000 to 6000 kv./cm.

It is hoped that the phenomena may be better understood when the theory which has proved successful in the case of polar crystals has been placed on a more general basis. The question is being further investigated by tests on pure long-chain hydrocarbon waxes of known constitution.

Authors' reply. Mr. G. G. Burleigh and Mr. Fleming-Williams have emphasized the complexity of the behaviour of plastics under mechanical stress. The strain is not a simple fnuction of stress alone. There may be more than one yield point, continuous flow at still higher stresses, and relaxation of stress

or strain under suitable conditions. Clearly, as Mr. Fleming-Williams states, a time factor must be associated with the elastic constants, and it is not difficult to see that this can take the form of a mechanical relaxation time, analogous to the electrical relaxation time discussed in our paper. Indeed, reference to the original papers mentioned by Dr. N. A. de Bruyne shows that Maxwell's relaxation time is such a time factor, and that its application to amorphous materials like plastics has been considered in some detail by Kühn. His work shows that the concept throws considerable light on the elastic behaviour of such bodies, but he finds it necessary to introduce several time constants differing widely in value, and the resulting complexity is so great that it is very doubtful whether the idea could be usefully applied to engineering testing technique. Empirical tests in conditions simulating those of actual practice seem likely to remain the most useful in connection with engineering design.

In reply to Dr. N. A. de Bruyne, we find that our time constants are of the same order as those calculated on the assumptions made by W. Kühn. The agreement is sufficiently close to justify the idea that there is a connection between the times of relaxation relevant to considerations of electrical and elastic properties, and we propose to examine the matter in more detail later (see p. 817, *infra*).

We agree with Dr. F. C. Frank that investigations of this kind are of importance on account of the insight which they give into the molecular mechanics of the materials. Indeed, we regard our paper as a record of the early stages of an investigation which will provide fundamental information about plastics of the kinds which Dr. Frank has enumerated, and although we have not employed all the concepts mentioned by him, our results obviously fall directly under his various headings. As far as plastics are concerned, we feel that the information so far available is but fragmentary. We hope in due course to make further contributions towards the details of the picture outlined by Dr. Frank.

Prof. Willis Jackson evidently feels that the absence of detail in the picture is at present one of its most conspicuous features, and one must agree that co-ordinated electrical and mechanical measurements are most desirable. Some time ago we planned such an investigation, but we have as yet nothing to report. Neither have we any new information about the synthesis of cross-linked molecules without the formation of undesirable condensation products.

Mr. A. Morris Thomas's values of intrinsic electric stength are very interesting. His experiments provide us with yet another approach to the structure of the materials, but here again it is clear that more experimental information is required. However, the results quoted are sufficiently striking. It is remarkable that when we are able to test the structure of the materials, apart from the more or less accidental hazards of ordinary commercial testing technique, there is so little difference between such widely different structures as polystyrene, polyethylene, phenol-formaldehyde resin and mica. The uniformity suggests a comparison with Kühn's contention that all materials have approximately the same elastic modulus. Ought one perhaps to use the term " intrinsic elastic modulus " in

his statement, and search for a connection with the "intrinsic electric strength"? It is an interesting point that both of these intrinsic values are obtainable by tests of very short duration, i.e., by impulse voltages lasting only a time of the order of a few micro-seconds in the one case, and by equally rapid elastic impulses in the other.

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MOLECULAR RELAXATION AND THE ELASTIC AND DIELECTRIC PROPERTIES OF PLASTICS

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ABSTRACT. The elastic modulus for various thermoplastics has been calculated by means of Maxwell's relation $\eta = G\tau$ (G being the modulus of rigidity), using the coefficients of viscosity, η, measured by observations of rate of flow, and the times of relaxation, τ, of their molecules deduced from observations of dielectric behaviour. For the phenolic thermoplastics the calculated values are practically independent of the state of the resin, from the hard to the very soft condition, and they lend some support to the suggestion put forward by W. Kühn that the true elastic modulus has nearly the same value for all materials, and that the wide differences in the elastic behaviour of materials like glass, rubber and plastics generally is due, not to differences in their true elastic modulus, but to differences in the rates at which stresses in these materials decay on account of molecular relaxation. The true modulus for materials with large molecules is considered to represent the total effect of molecular forces of many kinds, each with its own time of relaxation, and it is the distribution of these times of relaxation which determines the general character of the stress-strain relationship observed in ordinary practice. The values of τ deduced from dielectric behaviour refer to one group of forces only, viz., those due to the polar constituents of the molecules. Since Maxwell's simple equation appears to give the true modulus for the thermoplastics, we must suppose that in this case the same values of τ represent approximately all the molecular forces involved in elasticity and viscosity. For the benzyl alcohol resin the equation does not appear to give the true modulus, possibly because in this material there are relatively few polar groups, and therefore the time of relaxation representing the motion of these groups is less representative of the molecular forces as a whole.

In the discussion of our paper on "The dielectric properties of some thermoplastics", Dr. N. A. de Bruyne (p. 811, *supra*) drew attention to the work of W. Kühn [1], and raised the question whether the times of relaxation measured by observations of dielectric properties are in any way connected with those used by Kühn in order to explain the differences in the elastic behaviour of amorphous materials like glass, rubber and resins. Kühn's idea is that enormous differences in the stress-strain relationships ordinarily observed with such materials arise, not from differences in the modulus of rigidity, which he considers has roughly

the same value for all materials, but from differences in their times of relaxation. At the time we were only able to state, as a result of a preliminary consideration of the paper quoted by Dr. de Bruyne, that our values for the time of relaxation of the phenolic resins appeared to be of the same order as those derived from Kühn's idea. In the present note it is proposed to discuss the matter in more detail.

Kühn's work is based on a relation, first given by Maxwell, between the modulus of rigidity G_0, the relaxation time τ, and the coefficient of viscosity η of a material. The underlying conception is as follows. Consider a material which suffers a shearing strain. As a result of the forces between neighbouring molecules of the material, a stress proportional to G_0 is thereby established, but on account of the motion of the molecules the stress decays at a rate characterized by a time of relaxation τ, with the result that energy expended in producing the strain is dissipated as heat. In the steady state corresponding to continuous flow of the material, the decay of stress due to relaxation is just balanced by the increase of stress due to continued deformation. It can be shown that in these circumstances the actual value of the stress is equal to the product of $G_0\tau$ and the velocity gradient, and by equating the expressions for work done in terms of $G\tau$ and η, respectively, Maxwell's relation

$$\eta = G_0\tau$$

is obtained [2].

Kühn considers that the complicated elastic behaviour of materials like plastics, glass and rubber arises from the complicated motions of their large molecules, which cannot be represented by a single relaxation time, or even a single group of values, such as we have found necessary to account for their dielectric behaviour, but must be represented by several such groups differing widely, i.e. by several powers of ten, in mean value. The true modulus, as previously stated, is considered to be of the same order for all materials, but for materials like plastics, with large complicated molecules, this true modulus is considered to represent the total cohesive effect of molecular forces of many different kinds, some of which decay with great rapidity, and some extremely slowly. In any experiment the apparent modulus represents only those cohesive forces which are associated with time constants that are very large compared with the duration of the experiment, while any observed relaxation effects are due to those forces associated with times of relaxation of the same order as the duration of the experiment.

It is clear from these considerations that the times of relaxation measured by us and those discussed by Kühn both represent the motions of the same molecules, and it is to be expected that there will be some relation between them. We have suggested that our values of τ refer to rotation of the hydroxyl groups. Kühn's idea is that viscosity as determined by continuous flow involves molecular motions of many different kinds: translations as well as rotations; and rotations of molecules as a whole, involving also neighbouring molecules entangled with one

another, as well as rotations of small molecular groups, such as the hydroxyl groups in our resins. Corresponding to each of these modes of motion there are forces of cohesion and times of relaxation. Continuous flow involves the continuous production and continuous relaxation of shear stresses corresponding to all these forces and components of molecular motion, and Maxwell's simple equation becomes

$$\eta = \Sigma G_{n0} \tau_n,$$

where τ_n is the time of relaxation and G_{n0} the modulus of rigidity corresponding to the component denoted by the subscript n, and η is the measured coefficient of viscosity of the material. It is the sum of all the partial moduli, i.e. $G_0 = \Sigma G_{n0}$, which is considered to have roughly the same value (10^{10} to 10^{12} dynes/cm^2 for the elastic modulus E_0, where $G_0 = 0{\cdot}383\, E_0$) for all materials, but this value could only be observed in experiments in which the interval between the production of deformation and measurement of stress was negligibly small compared with all the values of τ, i.e. for vibrations of practically infinite frequency.

In order to fit our measured relaxation times into Kühn's argument it is obviously necessary to make some assumption about the distribution of relaxation times. Our experiments suggest the existence of a fairly narrow band, and the value obtained by us may be regarded as representing some sort of mean value for the whole band. Let us assume for the moment that the same value represents all the time constants involved in Kühn's equation. Then we have

$$\eta = \tau \Sigma G_{n0} = \tau G_0,$$

whence, making use of Poisson's ratio for a homogeneous material, we have

$$E_0 = \frac{\eta}{0{\cdot}385\tau}.$$

The values of the elastic modulus E_0 calculated by means of this equation and our values of η and τ are given below. It will be noticed that the values for all the phenolic resins are of the order 10^{10} dyne/cm^2 or 10^4 kg./cm^2, which is within the range of values stated by Kühn to hold for all materials. Moreover, all the values for any one of these resins are in agreement to about ± 10 per cent over a range of temperature in which tenfold changes of viscosity occur. The values agree well with that quoted by Kühn for colophony, viz., $2{\cdot}8 \times 10^4$ kg./cm^2, and there is therefore some prospect of relaxation times determined electrically being applicable to mechanical properties, at least for certain types of plastics.

The results for the benzyl alcohol resin require separate consideration. In this case the calculated modulus shows a systematic variation with temperature, and the smaller ones can hardly be considered to fall within the range mentioned by Kühn. We may go so far as to claim that the assumptions are verified for the phenolic resins, but fail for the benzyl alcohol one. This is rather curious when we consider that the benzyl alcohol resin is the one which most nearly obeys the Debye equations expressing electrical behaviour in terms of a single relaxation time, but the explanation is probably to be found in the smaller concentration

Values of elastic modulus (E), calculated from the time of relaxation (τ) deduced from dielectric properties,* and the coefficient of viscosity (η)

Resin	Temperature (°c.)	τ' (sec.)	η (poise)	E (dynes/cm^2)
Phenol-formaldehyde	57·5	$4{\cdot}5\times10^{-4}$	$7{\cdot}0\times10^{8}$	$4{\cdot}0\times10^{10}$
	59	2·7	3·97	3·8
	61	1·3	1·9	3·8
	62·5	0·67	1·1	4·3
	64	0·33	0·61	4·8
	66	0·19	0·31	4·2
o-Cresol-formaldehyde	34	4·7	2·55	1·4
	35	2·8	1·8	1·7
	36·5	1·4	1·05	1·9
	38·5	0·7	0·50	1·9
	40	0·35	0·29	2·2
	41·5	0·20	$0{\cdot}17_5$	2·2
p-Cresol-formaldehyde	47·5	4·7	4·0	2·2
	49·5	2·8	2·0	1·9
	51·5	1·4	1·0	1·9
	53·5	0·70	0·46	1·7
	55	0·35	0·285	2·1
	57	0·20	0·148	1·9
m-Cresol-formaldehyde	71·5	4·6	5·81	3·3
	73	2·8	3·60	3·3
	75·5	1·4	1·58	2·9
	77·5	0·70	0·86	3·2
	80	0·35	0·39	2·9
	82·5	0·20	0·19	2·5
m-5-Xylenol-formaldehyde	78	4·7	1·32	0·73
	80·5	2·8	0·64	0·59
	82	1·4	0·41	0·76
	84·5	0·71	0·20	0·73
	87	0·35	0·090	0·67
	89	0·20	0·057	0·74
Benzyl alcohol	37·5	5·3	0·88	0·43
	39	3·2	0·50	0·41
	41·5	1·6	0·20	0·33
	44	0·80	0·093	0·30
	47	0·40	0·035	0·23
	49	0·23	0·019	0·21

of OH groups in the benzyl alcohol resin. The intermolecular forces arising from these polar groups must be considered as relatively very large, and when there are many of them distributed throughout the material it is quite conceivable that

* The values of τ' are calculated by means of equations (3) and (6) in our paper *The dielectric properties of some thermoplastics*, p. 804, *supra*.

the viscosity of the material may arise almost entirely from stresses and relaxations associated with the motion of these groups, the viscosity associated with molecular motions having widely different time constants being negligible. When, however, the number of OH groups is comparatively small, as in the benzyl alcohol resin, the viscosity associated with mechanisms differing widely in time constant from that of the OH groups is no longer likely to be negligible, and the assumption therefore fails.

The actual values of the modulus are of considerable interest. As might be expected, the values for the *o*- and *p*-cresol resins are almost identical, with a mean value of $1{\cdot}9 \times 10^4$ kg./cm^2. The value for the *m*-cresol resin is rather larger, which doubtless arises from the fact that with this material cross-linkage is possible and does exist to some extent, thereby increasing the ability to resist deformation. The values for the resins made from phenol, *m*-cresol, and *m*-5-xylenol form a descending series, viz., 4·1, 3·0 and $0{\cdot}7 \times 10^4$ kg./cm^2. The additional methyl groups appear to lead to the formation of a structure less able to resist deformation.

This line of attack clearly provides a new approach to problems concerning mechanical properties, and one which may well repay further investigation.

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THE VARIATION OF SPARKING POTENTIAL WITH INITIAL PHOTO-ELECTRIC CURRENT: PART II

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ABSTRACT. A further discussion is given of the breakdown of a discharge-gap when subjected to intense ultra-violet radiation. The complete criterion for streamer formation as evolved for the writer's theory of spark discharge is adopted. This leads to a more rigorous solution of the problem than that presented in Part I, and it is shown that breakdown is probably initiated by midgap streamers for the larger photoelectric currents.

§1. INTRODUCTION

The observed lowering of sparking potential of a discharge-gap when the cathode is subjected to intense ultra-violet radiations has been explained in a previous article[1] (hereafter referred to as I) on the basis of the new theory of spark discharge[2]. The lowering is there ascribed to the accumulation in the gap of a positive-ion space-charge which is created as a result of cumulative ionization and depends on the intensity of the photo-electric current i_0 before the spark passes. This space-charge causes a variation of potential gradient in such a manner that the integral of the first Townsend coefficient α across the gap is greater than that for the externally applied field alone. The criterion there set for a spark to occur was that the integral of α across the gap should be the same as that to give breakdown of the uniform undistorted gap, viz., $\int \alpha\, dx = 18{\cdot}6$ for a 1-cm. gap at 760 mm. Hg. The greater the space-charge distortion the less need be the value of the externally applied field in order to produce a spark.

Subsequent to the writing of I much work has been done in the extension and application of the new theory of spark discharge, with the result that a more rigorous solution of the present problem can now be given. The original solution, though essentially correct, adopted a very much simplified criterion for breakdown. A spark was considered to be initiated by positive streamer formation at the anode. In the present article a more thorough analysis is made of the progress of the electron avalanche across the gap, and it will be seen that breakdown may occur by positive streamer formation in the mid-gap region for the larger photo-electric currents.

§2. THE CONDITION FOR POSITIVE STREAMER FORMATION

The radial field X_1 due to the positive-ion space-charge at the head of an avalanche after it has progressed a distance x from its origin is given by

$$X_1 = 5{\cdot}27 \times 10^{-7} \frac{\alpha_x e^{\int_0^x \alpha\, dx}}{(x/p)^{\frac{1}{2}}} \text{ volts per cm.,} \qquad \ldots\ldots(1)$$

where p is the air pressure in mm. Hg, α is the first Townsend coefficient, and α_x is the value of α at the point x where X_1 is to be determined[2].

The criterion for streamer formation has been discussed extensively elsewhere[2]. In brief, the criterion is that $X_1 = KX_x$, where X_x is the external field at x and K is a numerical factor. Originally the value $K = 1{\cdot}0$ was adopted, but subsequent experimental observations of the breakdown of several types of gaps would now indicate that $K = 0{\cdot}1$ is probably a more nearly correct value to give the condition for the minimum field necessary to streamer formation. Such a change in the value of K is found to produce but a minor change in the calculated sparking potential[2]. Substitution of $X_1 = 0{\cdot}1X_x$ in expression (1) leads to the equation

$$\int_0^x \alpha\, dx + \log_e \alpha_x/p = 12{\cdot}16 + \log_e X_x/p + \tfrac{1}{2} \log_e x/p. \qquad \ldots\ldots(2)$$

In the case of a uniform gap of length d, where breakdown for the minimum sparking field takes place by positive streamer formation *at the anode*, we obtain the equation

$$\alpha d + \log_e \alpha/p = 12{\cdot}16 + \log_e X/p + \tfrac{1}{2} \log_e d/p. \qquad \ldots\ldots(3)$$

This equation differs from that given in I (see equation (1), p. 548) only in the numerical value of the constant term. Both equations (2) and (3) can be solved for given gap conditions from a knowledge of the curves which relate α/p with X/p, and in this manner the breakdown field-strength for different gaps may be determined.

§3. THE SPACE-CHARGE DISTORTED GAP

It has already been indicated in I how the presence of a large photo-electric current leads to the accumulation of a positive-ion space-charge in the gap, and an equation is there developed for the equilibrium condition (equation (2), p. 551). This equation was solved by considering that $u_d = \int_0^d \alpha\, dx = 18{\cdot}6$, but subsequent work now makes it imperative that the strict criterion for the breakdown of the gap by streamer formation should be applied to this problem.

Owing to the involved nature of the expressions which give the field distribution in the space-charge distorted gap, and also the additional expressions for streamer formation, it is convenient to solve the problem for a particular i_0 by the choice of an arbitrary but plausible value of u_d in the manner described in I. Once the values of X and α across the gap have been determined, the radial field

X_1 produced by the positive-ion space-charge in a single avalanche may be calculated at various points in the gap from expression (1) of the present article. The value of X_1 can then be compared with the value of X, the existing space-charge distorted field. If the ratio X_1/X is greater than 0·1 at any point in the gap it is considered likely that a positive streamer will form and cause breakdown of the gap. Accordingly, for any particular values of d and i_0, a number of values of u_d must be chosen, and the solution of the equations gives the corresponding values of the externally applied potential V_d together with the variation of X and α in the gap. From the nature of the solutions for one or two cases a sufficient number of evaluations of the ratio X_1/X across the gap can be obtained to give a clear picture of the situation and to ascertain whether the criterion for streamer formation is fulfilled.

The solution of the space-charge equation (equation (2), p. 551) has now been performed in the case of a 1·0-cm. gap in air at 760 mm. Hg for $i_0 = 7{\cdot}5 \times 10^{-13}$ amp. per cm^2 with three different values of the externally applied potential (31 600, 30 700 and 29 800 volts respectively). The curves of figure 1 show the corresponding variations of V, X, α, $\int_0^d \alpha\, dx$ and $K = X_1/X$ across the gap. It is seen that in curve I for the *undistorted gap* the important increase in K occurs at the anode. In the case of the slightly distorted gap the important increase in K occurs at about 0·3 the way across. Thus for gaps distorted by space charge the breakdown of the gap is likely to occur by the formation of a mid-gap streamer.

The curves exhibit peculiarities which at first appear physically inconsistent. This is due to the indirect method of solution of the problem, and care must be taken in the correct interpretation of the curves. In order to solve the space-charge equation the values chosen for $u_d = \int_0^d \alpha\, dx$ were 16·4, 18·5 and 19·6 respectively for the curves I, II, III and correspond to potentials of 31 600, 30 700 and 29 800 volts. Thus it would appear that the solution predicts a smaller space-charge distortion for a larger applied V_d. However, all that the curves represent are solutions of the space-charge equation relating u_d, i_0 and V_d under steady-state conditions. They indicate that for a given i_0 a large u_d corresponds to a space-charge distorted gap and is thus associated with a lower V_d. This voltage is that which will maintain a condition of equilibrium in the gap for the given space-charge accumulation. It does not necessarily mean that this externally applied voltage will build up the calculated equilibrium space-charge, nor does it relate in a direct way to breakdown. The question here implied is answered only by an inspection of the various curves for K. It is at once clear that in each of the three cases a spark appears, either at the anode or in mid-gap, for the values of i_0, d and V_d considered. It is further apparent that with a sufficiently large space-charge distortion at equilibrium, the value of V_d is materially lower than that for the less distorted conditions and yet the criterion for breakdown is achieved. One may then logically enquire whether there is a lower limit to V_d as u_d is increased,

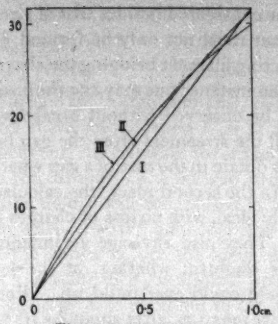

Figure 1 (*a*). V (volts).

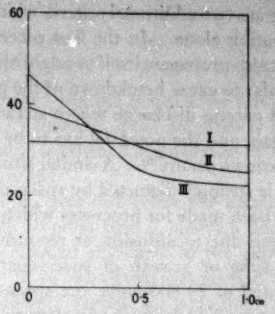

Figure 1 (*b*). X (volts per cm.).

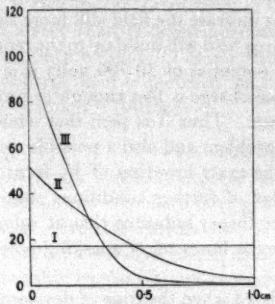

Figure 1 (*c*). α.

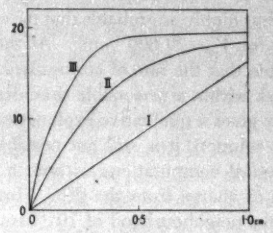

Figure 1 (*d*). $\int_0^x \alpha\, dx$.

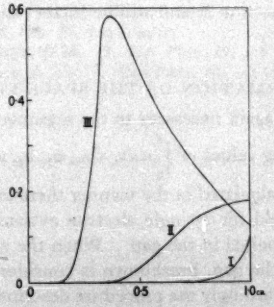

Figure 1 (*e*). K.

Figure 1. Curves to illustrate the calculated variations of (*a*) V, (*b*) x, (*c*) α, (*d*) $\int_0^x \alpha\, dx$. (*e*) $K = X_1/X$ for a 1 cm. gap at 760 mm. Hg. The curves I, II, III correspond to electron multiplication u_d of 16·4, 18·5, 19·6, and to potentials of 31 600, 30 700, 29 800 volts respectively.

though this is not apparent from the solution of the various equations. However, there are two additional criteria which must be considered besides that of streamer formation alone. In the first place a streamer must not only be formed, but it must also propagate itself to establish a conducting filament bridging the electrodes in order to cause breakdown of the gap. As an instance one may cite the positive-point corona discharge where streamers can be observed without breakdown of the gap, and the potential has to be raised till the streamers cross the gap before breakdown occurs [3]. A similar situation may obtain in the case of a gap where the field is strongly distorted by space-charge. In the second place, the calculations have been made for processes which are highly ideal, with no loss of charges from the gap due to diffusion or recombination. They also envisage an indefinitely long time of growth of space-charge. It is doubtful whether, at the lowest potential of 29 800 volts, the space-charge field could ever build up. For the increase in field due to the first "wave" of positive ions, i.e., after about 2×10^{-5} sec., is only 0·03 per cent as calculated in the approximate manner indicated in I, section 3. Subsequent waves of positive ions increase the field still more slowly. It is thus highly improbable that the space-charge field will build up to the requisite value for $V_d = 29\,800$ volts. At the higher potential of 30 700 volts it is conceivable that the rate of accumulation of space-charge is fast enough to produce a spark within a reasonable time despite losses. Thus it is seen that while the theory gives a qualitative explanation of the problem and also a possible quantitative solution, it is still not possible to fix the exact lowering of V_d from such theoretical computations without a knowledge of further conditions regarding losses of charge from the gap. However, the theory indicates that at values of i_0 in the neighbourhood of 10^{-12} amp. per cm^2 a lowering of sparking potential may be expected.

A definite lower limit for V_d may be calculated when the time of development of the field is considered as about 10^{-5} to 10^{-4} sec. The method of calculation has been described in I, section 3, and will be further discussed in the following section.

§4. THE TIME OF FORMATION OF THE SPACE-TIME CHARGE FIELD

Some modification is again necessary to the argument given in I concerning this topic. The increasing values of $\int_0^d \alpha\, dx$, viz., $u_1, u_2, u_3, \ldots\ldots$ for successive waves of positive ions is calculated in the manner there indicated. For each case the value of the radial field for a single electron avalanche is determined from expression (1) at various points in the gap. When the ratio $X_1/X = K$ is greater than 0·1 *at any point* in the gap, breakdown is considered to occur by positive streamer formation. Accordingly the procedure described in I must be modified to use this criterion for the spark in place of the original simplified criterion.

The potentials required to cause breakdown of a 1·0 cm. gap in a time corresponding to the crossing of the first "wave" of positive ions, i.e. $\sim 2 \times 10^{-5}$ sec.,

have been calculated from the modified viewpoint for various values of i_0 and are given in the following table :—

i_0 (amps./cm^2)	10^{-14}	10^{-12}	10^{-11}	10^{-10}	10^{-8}
V_d (volts)	31 600	31 600	31 350	30 650	28 850

For $i_0 = 10^{-11}$ amp. per cm^2, the value $K = 0{\cdot}1$ leading to streamer formation occurs at the anode when $V_d = 31\,350$ volts. However, if the potential is raised 0·2 per cent, the criterion for streamer formation is satisfied at a distance of 7 mm. from the cathode, i.e. a midgap streamer is formed.

The field distortion caused at a value of V_d near but below the breakdown value when $i_0 = 10^{-8}$ amp. per cm^2 is already so great that K shows a decrease near the anode before the value $K = 0{\cdot}1$ is reached anywhere in the gap. As soon as a value of V_d is applied which in one wave of positive ions gives $K = 0{\cdot}1$, this value of K is achieved in the midgap region. Hence, for such high values of i_0, breakdown takes place via a midgap streamer.

It is seen that this treatment of the problem leads to breakdown at a potential above a very sharply defined threshold, and differs markedly from the case with the equilibrium field. The method has the advantage in that the growth of the space-charge field is pictured, and one can determine at what point the breakdown criterion is fulfilled.

§ 5. ACKNOWLEDGEMENTS

The writer wishes to express his appreciation to Professor L. B. Loeb, whose suggestions and criticisms have greatly contributed to the solution of the present problem. He also thanks Dr. W. R. Haseltine for his valuable discussions relevant to the solution of the equilibrium space-charge equation. The grant of a Fellowship by the Commonwealth Fund is again most gratefully acknowledged.

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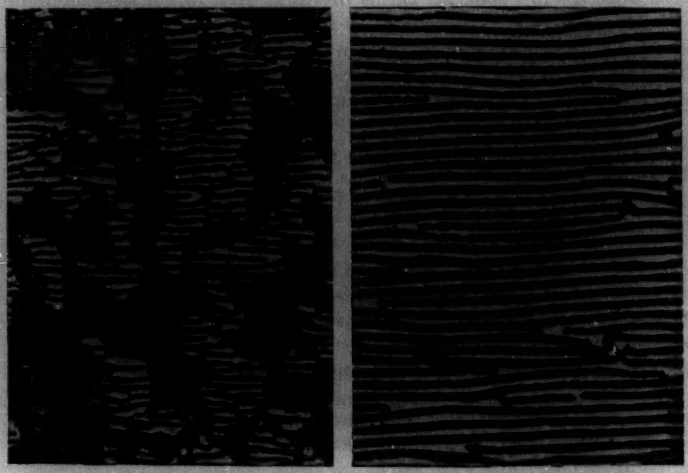
DEMONSTRATION

CONTROLLED FLOCCULATION. *Demonstrated* 8 *March* 1940 *by* DOROTHY L. TILLEARD, B.Sc., F.Inst.P., Paint Research Station.

THIN films of pastes consisting of fine solid particles dispersed in a viscous liquid show marked changes in dispersion when subjected to a slow shear. As



(A) ×220. (B) ×500.

Cylindrical flocculates produced by shearing pastes of carbon black in linseed oil.
(A) Partial development. The dark areas in the photograph indicate dispersed material.
(B) Complete flocculation. The film in this condition shows diffraction spectra.

shown in the figures, the particles become packed together in long cylindrical flocculates of such fineness and regularity of spacing as to give bright diffraction spectra.

OBITUARY NOTICE

ROOKES EVELYN BELL CROMPTON

COLONEL ROOKES EVELYN BELL CROMPTON, C.B., F.R.S., Hon. Colonel 11th Batt. Royal Engineers, who died on 15 February 1940, at Azerley Chase, Ripon, at the age of 94, was in many respects a pioneer in the technical advance that characterized his time. To the world at large he was best known for the part he took in the industrial development of electric lighting and mechanical road traction, but he was at heart a soldier, and his whole career reveals his energies distributed between engineering undertakings and military affairs. He was born at Sion Hill, near Thirsk, on 31 May 1845, where his father, who had claims to be described as a scholar, a traveller and a diplomatist had settled down as a country squire. His mother, the beautiful daughter of Sir Claud Alexander, was a famous amateur pianist, a pupil of Mendelssohn. To complete his natural endowments, he was—through the family of his grandmother—in descent from John Evelyn of Wootton.

He has told us of the most noteworthy event of his early life—his visit in 1851 to the Great Exhibition in Hyde Park, where for the first time he saw the machine tools then coming into use in engineering shops. The special Engineering Train in which he had travelled to London from Thirsk was drawn by six locomotives. In the following year he went to school at Sharow near Ripon, where one of his mates was " a sallow-faced boy named Dodgson " (Lewis Carroll). The course of events was, however, in 1854, severely broken. His father's regiment of militia was ordered to Gibraltar, and there the family took up their quarters. Shortly afterwards, Gibraltar happened to be a port of call for H.M.S. *Dragonfly*, commanded by his mother's cousin, with the result that the boy was taken on board and enrolled as a cadet in the Royal Navy, at the age of ten. The rest of the story is told in his " Reminiscences ", where also will be found an account of his return to England, his subsequent army life in India, where he did so much towards the development of motor transport, and his sudden blossoming into fame in Paris in 1878, to his own surprise, as a leading authority on electric lighting. Thus early in the electrical industry he recognized the value of electric lighting for advertising purposes and he began to produce "sets" of generator equipment, by associating with makers of the Gramme machine. By December 1880, the first Bürgen machine was completed at his works in Chelmsford, which he had founded in 1878. In 1881 he was appointed Engineer to the Edison-Swan Company and took an active part in the struggle for Provisional Orders and in the contests through Parliamentary Committees following the Electric Lighting Acts.

In England money could not be found for central station enterprises, but

he secured a contract for the lighting of part of Vienna, at the completion of which he returned to London and, in 1886, inaugurated the Kensington Court Electric Supply Company. The generating station was on the site of the estate of Sir Albert Grant (Baron Grant) which had recently come into the market. He made special use of a subway that had been constructed under the estate, and he built in Kensington Court a house he designated Thriplands, for his own dwelling. This was conveniently near to the Royal School of Mines in Exhibition Road, where meetings of the Physical Society were at that time held. He was elected a Fellow of the Society in 1889 and was a member of the Council from 1899 to 1900. He desired at all times to keep in touch with the advance of physical science, but his outlook was technical and commercial, and it is significant that he never contributed a paper to the *Proceedings of the Physical Society*. Yet his pen had not been idle. By 1900, the turning point in his career, he had already described at a meeting of the Institution of Mechanical Engineers, experiments he had carried out in India on road traction. In 1880 he produced a valuable pamphlet on "The Electric Light for Industrial Uses," and in 1891 his famous paper, read before the Institution of Civil Engineers, on "The Distribution of Electrical Energy". This was supplemented in 1894, by his paper at the Institution of Electrical Engineers on "The Cost of Electrical Energy". It cannot be supposed that his interest in the familiar Crompton regulator arc-lamp and in the Crompton dynamo had ceased. His writings show, however, that from 1900 to the end of his writing days, his themes, with one exception, were concerned with road transport. The exception was his James Forrest Lecture in 1905 on "Unsolved problems in Electrical Engineering". This followed his Presidential Address in 1903 to Section G of the British Association, on "Problems of Modern Street Traffic".

The incidents that in 1900 gave a new bent to his activities are well known. A small body, the South African Detachment of Electrical Engineers (R.E.) Volunteers, trained for search-light operation, coast defence and mining, telephony and telegraphy, was, in March of that year, embarked under his command, and by 7 May they were at Bloemfontein with Lord Roberts. Upon his return to England, Crompton became Chairman of the Kensington and Knightsbridge Company. He was an original member of the Automobile Club, where in the late autumn of his life he vanquished many a younger player at squash racquets. He was President of the Institution of Electrical Engineers in 1895, and again in 1908. He also served as President of the Institution of Automobile Engineers and of the Institution of Junior Engineers. He married Miss Elizabeth Gertrude Clarke, of Ripon. In June 1931 they celebrated their diamond wedding. There were, of the marriage, two sons and three daughters. Mrs. Crompton died on 27 November 1939.

ROLLO APPLEYARD

REVIEWS OF BOOKS

Thermodynamics and Chemistry, by F. H. MACDOUGALL. Third edition. Pp. viii + 491. (New York: John Wiley and Sons; London: Chapman and Hall, Ltd.) 30*s.* net.

The first and second editions of this book were among the soundest introductions to thermodynamics available for the student who required clear ideas without "philosophy", and preferred help with his mathematics. The third edition is a completely rewritten introduction, taking account of the change in outlook which has come about in the last few decades, but still designed to appeal to the student (of chemistry or physics) whose main purpose is to learn how to use this valuable tool. About half the book is devoted to expounding the principles and deducing the familiar fundamental formulae, and the other half to those applications sometimes grouped together as physical chemistry. In the treatment of solutions, we notice that the Debye-Hückel theory is expounded at some length.

One of the most useful parts of the older book was that dealing with the application of the phase rule, and in particular the deductions as to the behaviour of liquid mixtures. It is good to note that the latter has been retained practically unchanged. The last chapter, entitled "Third Law of Thermodynamics. Radiation. Statistical Mechanics", is the one in which the difference from the older "classical" thermodynamics is most striking and which must have been the most difficult to write, but it ably maintains the standard of exposition set by the author in the rest of the book. In its new form it will be as widely used as ever. J. H. A.

Notes on the Preparation of Papers for publication in the Journal of Hygiene and Parasitology, by [the late] G. H. F. NUTTALL. Pp. 62. (Cambridge: University Press, 1940.) 4*s.* 6*d.*

These notes, though directed primarily to contributors to two particular journals are intended to be of interest and value to writers for publication elsewhere. Much good advice on the preparation of manuscript is given, and there are detailed instructions on proof correction. A good deal of space is devoted to such matters as the logical arrangement of the paper in sections and suggestions on the use of abbreviations.

There is a section on "style", in which the subsection on punctuation contains much sensible advice. It would appear that the faults of physicists differ from those of biologists, for two of the commonest faults found in manuscripts submitted for the *Proceedings of the Physical Society* are not mentioned at all. They are the incorrect use of hyphens and the misuse of "due to". On the other hand, some errors are exposed to which physicists are not prone. Nevertheless the notes are well worthy of perusal, which need occupy little more than an hour. From the technical point of view, as would be expected, the production is excellent. J. H. A.

Sir John Cunningham McLennan; A Memoir, by H. H. LANGTON. With a Chapter on his *Scientific Work*, by E. F. BURTON. Pp. 123. (Toronto: The University Press; London: Sir Humphrey Milford at the Oxford University Press, 1940.) 11*s.* 6*d.* net.

This brief but admirable memoir sketches the fascinating story of the life of a singularly attractive personality. His career was successful, in the highest sense of the word, and he owed much of his success to energy, drive, clearsightedness, and to the possession of those old-fashioned virtues of strict integrity and directness of purpose. He had qualities of ruthlessness, but he never expected of others what he was not prepared to do himself. And he combined these qualities with a capacity for affection which became more apparent with increasing years and which made him a most charming and thoughtful companion. He was a born teacher and researcher, gifted with a power of singularly lucid exposition, and with untiring patience in following up the faintest clues. Had he accomplished nothing else than the building, *ab initio*, of the great laboratory which is honoured by bearing his name, it would have been accounted an achievement sufficient for any one man's life-work.

The more so, that, in the pursuit of that object, McLennan had not only to provide the knowledge which should serve to build and equip the laboratory, and to direct its work, but also, in searching for the funds, to exert to the full those arts of the diplomatist and politician which he possessed in no small degree.

But he crowded much more into the tale of his sixty-eight years. His work for the Admiralty during what we were wont to call the War years was of signal service to the Empire. In this work, it may be noted, he showed his political insight by insisting that as a professor in charge of scientific work he should be recognized as equal in rank with an admiral. He thus short-circuited all sorts of departmental delays by being able, in virtue of his position, to report direct to the First Sea Lord.

After his retirement from the Toronto Chair, he devoted his overflowing energies to the problem of radium-beam therapy, and to the services of various international committees. It was after attending a meeting of a committee of the International Bureau of Weights and Measures, that death, sudden and painless, overtook him.

It is all to the good that the story of McLennan's life should be placed on record. The book will be read with deep interest by his many friends, and will be an inspiration to all students of science. A. F.

The Calculation and Design of Electrical Apparatus, by W. WILSON, D.Sc., M.I.E.E. Second edition. Pp. xiii + 230. (London: Chapman and Hall, Ltd., 1940.) 10*s.* 6*d.*

This book is written for the assistance of the electrical engineer. The term electrical apparatus, as used by the author, is intended to exclude machines and transformers, and to include switch gear, control gear, protective equipment, windings, solenoids and condensers. Within these narrow and specialized limits the treatment is clear and to the point. Tables of data, and practical formulae, are applied to fully worked out examples. The physicist will find some interesting and probably unfamiliar illustrations of well-known principles; for instance, that in a short circuit the switch gear and bus bars may have to stand up to electrodynamic forces amounting to several tons weight. D. O.

General Physics for Students of Science, by ROBERT BRUCE LINDSAY. Pp. xiv + 534. (New York: John Wiley and Sons; London: Chapman and Hall, Ltd., 1940.) 22*s.* 6*d.* net.

General Physics is a title which will prove somewhat misleading to the majority of English readers, accustomed as they are, in English scientific literature, to the association of the term with that part of the subject dealing with properties of matter. In this book however, Prof. Lindsay endeavours to cover the whole field of Physics, and the purpose, to quote the author, is twofold, viz., " to serve as a basic introductory text-book for science students who have had mathematics through elementary calculus, and also to provide an intermediate and more rigorous course for such students as have already taken an elementary, descriptive course in physics ".

The book is divided into five main parts. Part I deals with the method of physics and the development of physical theories, and in a very brief but comprehensive history of the subject the author traces its progress through the centuries, and emphasizes how more elaborate theories have led to more precise experimental technique. In Part II the author gives a particularly careful presentation of the fundamental concepts of mechanics, an essential but oft-neglected preparation for the physics student. It is a surprise to find no mention whatever of viscosity, even in the theory of damped oscillations, yet space is found for reference to Brownian motion and the molecular theory of liquids. Part III is devoted to *Heat*, and contains chapters on the kinetic theory and thermodynamics. The chapter on *The Transfer of Heat* is noteworthy for the attempt to supplant the usual qualitative reference to heat convection by a simple, yet illustrative, mathematical analysis. The *Electricity* section, Part IV, covers a wide field; both alternating currents and electrical discharge through gases are dealt with; radio, however, receives no specific mention. Prof. Lindsay uses the gauss for the unit of field intensity, and not the oersted, the latter retaining its old significance as the unit of magnetic reluctance. Acoustics, optics and electromagnetic radiation are embodied in the concluding section of the book. In the chapter on *Acoustics* the author does well to cover, within the limited space available, the many recent developments of the subject, without appearing to be just cataloguing " effects and facts ". The last chapter in the book is mainly theoretical in aspect, the quantum theory and the theory of relativity both receiving adequate consideration.

The book is well produced, line-diagrams only are included, and its value is considerably enhanced by the addition of sets of well-chosen examples (without numerical solutions), each set based on the subject matter of the preceding chapter.

R. W. B. S.

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